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## RESEARCH ON CHARACTERISTICS OF TRANSITION ELEMENTS IN SOLUTION

### 1. Studies on rhodium chemistry

by CLARA BERECKI-BIEDERMANN

### 2. Studies on ruthenium chemistry

by FELIPE BRITO

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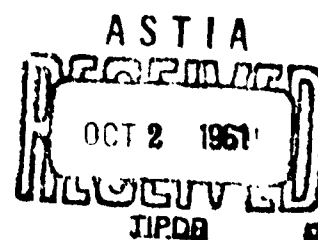
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LARS GUNNAR SILLÉN  
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TECHNICAL REPORT

CONTRACT NO AF 61(052)-181



MONITORING AGENCY DOCUMENT NO.

ASTIA DOCUMENT NO.

RESEARCH ON CHARACTERISTICS OF TRANSITION ELEMENTS IN  
SOLUTION

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TECHNICAL REPORT

CONTRACT NO. AF 61(052)-181

The research reported in this document has been sponsored by the  
AIR FORCE CAMBRIDGE RESEARCH CENTER of the AIR RESEARCH and DEVELOPMENT  
COMMAND, UNITED STATES AIR FORCE, through its European Office.

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The technical report consists of two independent units and it has been thought convenient to give them separate numbering of pages, figures, and references.

## Abstract

Rhodium

→ A method is described for the preparation of halogenide-free rhodium(III) perchlorate and sulfate solutions. As starting material rhodium chloride or ~~preferably~~ <sup>wza</sup> rhodium bromide <sup>can be used</sup> can be used. The halogenide was removed by means of ozone, which oxidizes free (not complex-bound) halogenide to halogen.

For the analysis of total Rh, a method is proposed, based on reduction of the metal by passing  $H_2$  through the solution at  $90^\circ C$ . The filtrate can afterwards be conveniently analyzed for excess  $H^+$ , for total anions by ion exchanger and for ~~any~~ other constituents. The analytical values for Rh so obtained, agree to  $\pm 0.15\%$  with those found using the earlier method of Gilchrist and Wichers.

(Preliminary studies on the hydrolysis of rhodium(III) in perchlorate solutions at  $25^\circ C$ , by emf and spectrophotometric measurements, indicate that a single species predominates, probably with  $1.75 \pm 0.1$  <sup>+0.1</sup> OH<sup>-</sup> bound per Rh atom. Possible ions would be  $Rh_3(OH)_5^{4+}$ ,  $Rh_4(OH)_7^{5+}$  or  $Rh_5(OH)_9^{6+}$ .

The experimental conditions ~~have been~~ <sup>investigated</sup> for the quantitative oxidation of Rh(III) to Rh(V) by means of <sup>O<sub>3</sub></sup> ~~ozone~~ in perchlorate and sulfate solution. The oxidation number +5 of the species formed has been determined by iodometry.

Extinction curves for <sup>Rh</sup> rhodium(III) in perchlorate, sulfate and chloride solutions, and for Rh(V) in sulfate and perchlorate solutions are given.

Ruthenium

As a necessary preliminary to equilibrium studies on the hydrolysis of ruthenium(III) and ruthenium(IV) synthetic and analytical methods have been studied and several modified or new methods developed.

→ <sup>Ru</sup> Ruthenium(IV) sulfate or perchlorate solution <sup>and</sup> is prepared by reducing  $RuO_4$  with  $H_2O_2$  in dilute  $H_2SO_4$  (or  $HClO_4$ ) and separating the ruthenium(IV) cations from complex anions with a cation exchanger. <sup>Ru</sup> Ruthenium(III) sulfate solution <sup>were</sup> prepared by reducing  $RuO_4$  with  $SO_2$ , removing excess  $SO_2$  and decomposing the sulfite complex.

Total ruthenium was determined by weighing as metallic ruthenium. The reduction can be done with metallic Mg in the solution; this method is applicable even where other methods fail.

→ A redox titration method is proposed suitable for determining total Ru in ~~very~~ dilute solutions. A known excess of cerium(IV) sulfate in 2 M  $H_2SO_4$  is added, the  $RuO_4$  <sup>boiled off</sup>, and the remaining Ce(IV) back-

titrated with Fe(II) + ferroin. This method was used to prove the assignment of the valencies Ru(IV) and Ru(III).

The total analytical concentration of  $H^+(H)$  was determined by titration with NaOH, the ruthenium either being removed on an ion exchanger, or by adding acetylacetone or, alternatively, by titrating to the point where it is completely precipitated as hydroxide. The results with these three methods seem to agree well.

Spectral absorption curves are given for the important forms of Ru met with. For Ru(IV) the absorption may be used for quantitative determination.

A preliminary study of the hydrolysis of Ru(IV) indicates that, at least in solutions between 0.04 and 3 M in  $H^+$ , it is present in the form of a single species.



## Studies on rhodium chemistry

Clara Berecki-Biedermann

### Introduction.

In the last decade a considerable number of complicated ionic equilibria, especially those of hydrolysis, have been studied in this laboratory. A review of the recent results was given by L.G. Sillén<sup>1</sup> in 1959. Much work has been devoted to finding both suitable experimental methods, and numerical and graphical approaches for the evaluation of the data. The success of these investigations depends to a large degree on having reliable and sufficiently accurate methods of preparing and analysing the solutions studied.

At the start of the present investigation it was realized that in the case of rhodium solutions special problems have to be solved. Very few data can be found on the ionic equilibria involving rhodium and as a consequence much effort had to be made to prepare solutions of sufficient purity and to analyze them with high accuracy.

The main difficulty in studying the metals of the platinum groups is that the ions of these elements often react very slowly at temperatures lower than about 100°C and therefore, methods for preparation and analysis which are successful with most other metals frequently cannot be applied.

This difficulty might be overcome by working above 100°C at elevated pressure but then one must be prepared to devote considerable effort to developing a suitable experimental technique.

In the course of the present work indications have been found that the inertness of the rhodium species is mainly confined to reactions involving substitution of ligands, e.g.  $\text{Cl}^-$  by  $\text{ClO}_4^-$ . On the other hand rhodium proved to react reasonably rapidly in several redox processes. The difference between the rate of the substitution and that of the redox reactions has been of great value in developing convenient methods of preparations and analysis.

There are reasons to believe that the results presented here might prove to be of some value for the study of ionic equilibria involving some other metals that belong to the platinum group or are near to it in the periodic table.

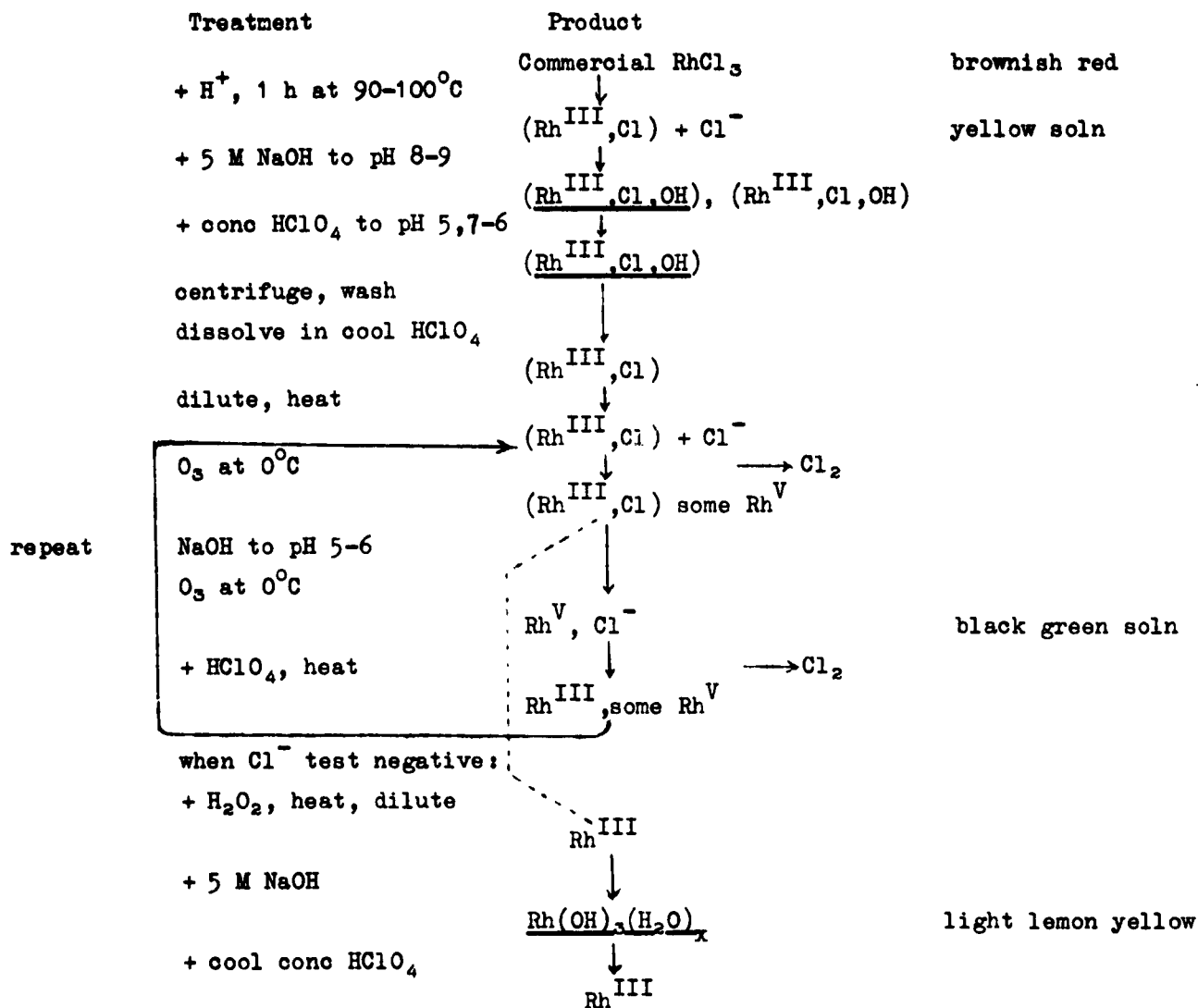
Preparation of halogen-free rhodium(III) perchlorate and sulfate solutions.

This part of the work has already been presented in Technical Note No 2 which is attached as an Appendix and describes the method of preparation and the test for  $\text{Cl}^-$ .

After Technical Note No 2 was submitted several lots of concentrated Rh(III) perchlorate solutions have been prepared according to the proposed "ozone method". In connection with this work improvements were made on two details which have been worked into the Scheme.

1) The reduction of Rh(V) to Rh(III) is made before the last precipitation step because the excess of the reducing agent ( $\text{H}_2\text{O}_2$ ) is then easily removed. (If the final perchlorate solution is heated with  $\text{H}_2\text{O}_2$  sometimes  $\text{Cl}^-$  seems to be formed.)

2) It is essential when testing for  $\text{Cl}^-$  that the  $\text{Rh}(\text{OH})_3(\text{H}_2\text{O})_x$  precipitate should be of a light lemon yellow color. From concentrated perchlorate solutions a dark brown basic perchlorate is often formed. The presence of the perchlorate in the precipitate makes the chloride test unreliable. The formation of basic perchlorates may be avoided by first adding so much NaOH that the soluble hydroxo complex is formed which is then decomposed with dilute  $\text{HClO}_4$ .

Scheme of preparation

In this diagram  $(\text{Rh}^{\text{III}}, \text{Cl}, \text{OH})$  stands for a solid containing these constituents in unspecified proportions and  $(\text{Rh}^{\text{III}}, \text{Cl}, \text{OH})$  or  $(\text{Rh}^{\text{III}}, \text{Cl})$  for complexes in solution

$\text{Br}^-$  is definitely preferred to  $\text{Cl}^-$  as starting material

$\text{HClO}_4$  may be replaced by  $\text{H}_2\text{SO}_4$

### Analysis of rhodium(III) solution.

In ohloride, sulfate and perchlorate solutions the stable oxidation state of rhodium is generally supposed to be Rh(III), since the solid rhodium salts obtained by crystallisation from solutions containing these anions always proved to contain Rh(III)<sup>2,3</sup>. Some polarographic evidence has also been obtained recently<sup>4</sup> for the presence of Rh(III) in Cl<sup>-</sup> solutions. The absence of any reducing or oxidizing substance in our stock solutions could be proved by the fact that they did not consume nor liberate any detectable amounts of I<sub>2</sub>. The test for the oxidizing agent was made in O<sub>2</sub>-free solutions in a CO<sub>2</sub> atmosphere.

In order to study hydrolysis and other ionic equilibria we need to know

- 1) the total concentration of Rh, B,
- 2) the "analytical" concentration of hydrogen ions, H, i.e. the hydrogen ion concentration assuming no hydrolysis takes place
- 3) the concentration of Na<sup>+</sup>, if present, and
- 4) the  $[\text{ClO}_4^-]$  (or  $2[\text{SO}_4^{2-}]$ ) = 3 B + H + [Na<sup>+</sup>]

Perchlorate, sulfate and chloride solutions of rhodium were investigated. The common starting material for all solutions was MacKay's RhCl<sub>3</sub>(H<sub>2</sub>O)<sub>4</sub>. Some of the perchlorate and sulfate solutions used had been prepared and analyzed before the "ozone method" had been worked out and thus contained some chloride.

### Total Rh via sulfide

The Rh content of the solutions was determined according to Gilchrist and Wichers<sup>5</sup>. Their method is beyond doubt the most reliable of those described in literature. In the following the procedure is given with more detail than in ref. 5.

A weighed amount of the stock solution (2-5 g) was diluted to 150-200 ml in a beaker and boiled with conc. HCl (5-10 ml) for 15-20 min. The presence of excess Cl<sup>-</sup> is essential; preliminary experiments have shown that - as in the case of rhodium sulfate solutions - precipitation from ClO<sub>4</sub><sup>-</sup> solutions by H<sub>2</sub>S was not complete.

In some experiments 5-10 ml 4M NaCl was added instead of HCl. Then, however, a detectable amount of Na<sub>2</sub>SO<sub>4</sub> remained adsorbed on the sulfide precipitate and was hard to remove.

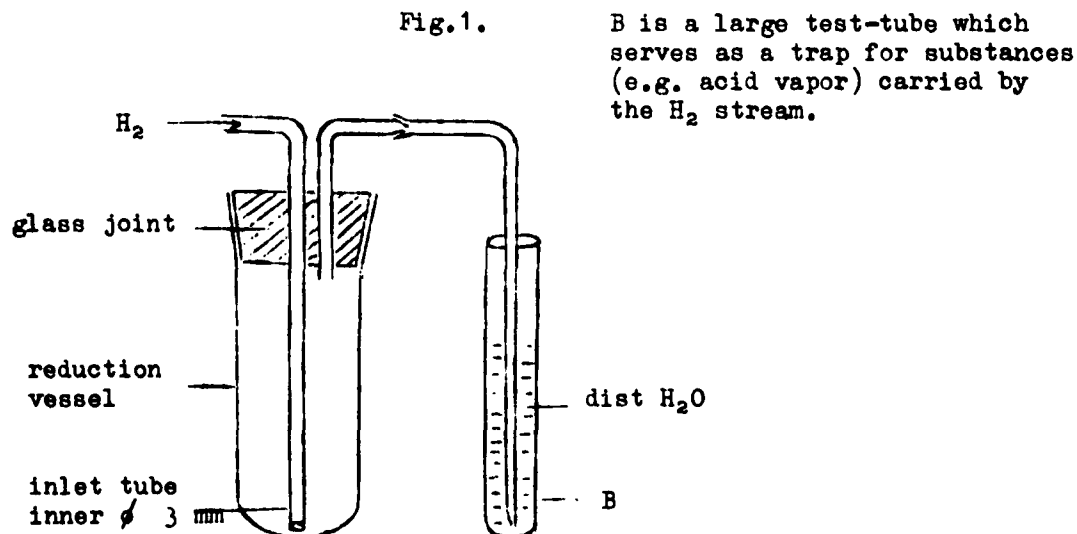
On adding Cl<sup>-</sup> and boiling the color of the solution turned from yellow to dark rose. A rapid stream of H<sub>2</sub>S, taken from a cylinder, was passed first through dist. H<sub>2</sub>O and then into the boiling solution for half an hour.

The solution was then allowed to cool to room temperature, still in a stream of  $H_2S$ . The voluminous precipitation settled rapidly. The supernatant liquid was colorless and remained so even after evaporation to 25 ml. The precipitate was collected on a filter paper ('Munktells No OOH', average ash per circle 0.03 mg) washed with 15 - 25 ml of diluted  $H_2SO_4$  (2.5 + 97.5) and finally with 15 - 25 ml of  $HCl$  (1 + 99). The precipitate was transferred to a weighed porcelain crucible of the Rose type ("Haldenwander 79 C-0") and a few drops of  $NH_4Cl$  added. It was dried at  $120-130^\circ C$ , charred at  $400^\circ C$  then ignited at  $750^\circ C$  in an electric oven and finally reduced in a stream of  $H_2$  at light red heat. The metal was cooled in a stream of  $H_2$  and weighed as metallic Rh. The reduction was repeated twice but the change in the weight was less than 0.05 mg.

#### Total Rh by $H_2$ reduction

Other Rh determinations were carried out in a slightly different way. Use was made of our experience, reported earlier in connection with the procedure for testing for  $Cl^-$  in Rh-solutions (see Appendix). Rh(III) can easily be reduced from  $ClO_4^-$ ,  $SO_4^{2-}$  or  $Cl^-$  solution by passing  $H_2$  through it. For the reduction we used and recommend a simple all-glass apparatus of the following design which is self-explanatory.

Fig. 1.



A weighed amount of stock solution was transferred to the tube, diluted to 20 ml and placed in a waterbath.  $H_2$  was passed through the solution and the temperature of the bath was raised. The color of the solution became slowly brownish-red, darkened slightly and above  $90^\circ C$  quickly turned

green. At the same time metal deposition began in the form of fine, bright lamels or as a fine gray powder, depending on the concentration of Rh in the solution. The rate of reduction was greatly increased owing to auto-catalysis when a visible amount of Rh metal had precipitated. After a while the color faded and finally a clear, colorless solution and metallic Rh remained. The metal was collected on ashless filterpaper washed with dist. water and ethanol. The deposited Rh tended to form a thin film on the walls of the vessel and on the inlet tube, especially at the solution surface.

The adherent metal could easily be wiped off with a piece of ashless filter paper. Together with the main part of the filtered metal residue it was ignited first in air and then in  $H_2$  and finally cooled in  $H_2$  and weighed.

If the reduction  $Rh(III) \rightarrow Rh(O)$  is made by  $H_2$  the step involving the precipitation and washing of rhodium sulfide is eliminated and thereby errors due to absorption can be avoided. Analyses made by the two methods are compared below in Table 1.

Table 1.

Sulfide method			H <sub>2</sub> method		
a: stock solution weighed in g					
b: weight of metallic Rh mg					
c: mg Rh/g stock solution					
a	b	c	a	b	c
1.8108	51.5 <sub>7</sub>	28.48	3.0216	86.3 <sub>7</sub>	28.58
3.6632	104.8 <sub>7</sub>	28.63	4.1268	116.8 <sub>6</sub>	28.32
6.0824	172.8 <sub>7</sub>	28.42			
	av.	28.51		av.	28.45

#### Total anions and H.

To analyze for H and  $[Na^+]$  the Rh must first be removed from the solution. This can be accomplished in the simplest way, by reducing it with  $H_2$ ; the reduction proceeds rapidly under the experimental conditions described above. It is most convenient to use aliquot parts of the collected filtrate and water-washings obtained during the Rh determination by the  $H_2$  method.

Titration of the filtrate with standardized NaOH gives the sum:  $H + 3B$ .

Another aliquot of the filtrate is passed through a cation exchanger (Dowex 50) in the hydrogen form. The eluate titrated with standardized NaOH yields e.g.  $[\text{ClO}_4^-]_{\text{total}} = 3 \text{ B} + \text{H} + [\text{Na}^+]$ .

The filtrate can also be used for the direct(separate)determination of the anion present ( $\text{SO}_4^{2-} \rightarrow \text{BaSO}_4$ ,  $\text{Cl}^- \rightarrow \text{AgCl}$ ).

### Hydrolysis of rhodium(III) ion. Preliminary results.

#### Earlier work.

The first attempt to study the hydrolysis equilibria of the Rh(III) ion was made in 1938 by Grube and Autenrieth<sup>6</sup>. These authors measured the acidity of a series of  $\text{RhCl}_3$  solutions with a glass electrode and explained their results obtained in dilute rhodium solutions by assuming the formation of the species  $\text{RhOH}^{2+}$ , whereas at higher Rh-concentrations evidence was found for the presence of other species of unidentified composition. In connection with an investigation on electroplating, Grube and Kesting<sup>7</sup> (1933) concluded from the fact that 1 mole  $\text{Rh}(\text{OH})_3(\text{s})$  can be dissolved in 1 mole  $\text{HClO}_4$  that the ion  $\text{Rh}(\text{OH})_2^+$  is present in highly hydrolyzed solutions.

C.K. Jørgensen<sup>8</sup> in 1956 in a preliminary experiment titrated a 0.01 M Rh(III) solution containing 1.0 M  $\text{NaClO}_4$  with NaOH (and  $\text{HClO}_4$ ) by measuring the  $[\text{H}^+]$  with a glass electrode. On the basis of these data Jørgensen concluded that in the  $\log \text{H}^+$  range, -2 to -4 the predominant species formed by hydrolysis contains two OH groups bound to one rhodium atom, thus it has the composition  $[\text{Rh}(\text{OH})_2^+]_n$  where n is an integer. His spectrophotometric studies also gave some support to this interpretation of the emf data.

On the basis of potentiometric (with glass electrode) and conductivity titrations on a dilute solution (1.2 mM) of  $\text{Rh}(\text{ClO}_4)_3$  Forrester and Ayres<sup>9</sup> (1959) suggest that besides the mononuclear  $\text{RhOH}^{2+}$  ( $K_1 = 3.7 \cdot 10^{-4}$ ) a polynuclear species containing at least two or three rhodium atoms is present in appreciable amounts in the hydrolyzed solutions.

#### Choice of method.

Few methods of investigation may be expected to yield data sufficiently accurate for the determination of the composition of the hydrolysis products and of the corresponding equilibrium constants.





where RE denotes the half-cell



The emf of the cell with the glass electrode can be written at 25°C

$$E_1 = E_{01} + 59.15 \log h - E_j \quad (1)$$

and that of the cell with the quinhydrone electrode will be

$$E_2 = E_{02} + 59.15 \log h - E_j + \delta \quad (2)$$

In (1) and (2)  $E_{01}$  and  $E_{02}$  denote constants, and  $E_j$  is the liquid junction potential at the junction solution S | 3 M NaClO<sub>4</sub>. The  $E_j$  values have been taken from the work of Biedermann and Sillén<sup>11</sup> who found that the equation  $E_j = 16.7 h \text{ mV}$  describes their data with a good approximation.  $\delta$  is a small correction term which takes into account the basic nature of quinone<sup>12</sup>.

The measurements were carried out as usual in this laboratory in the form of potentiometric titrations. In each series of measurement B was kept constant.

#### Experimental details of the emf measurements.

The emf measurements were made at  $25.00 \pm 0.01^\circ\text{C}$  in a paraffin oil thermostat.  $E_1$  was determined by a valve potentiometer Radiometer PHM4 Copenhagen, with a reading accuracy of  $\pm 0.1 \text{ mV}$  and  $E_2$  was measured with an accuracy of  $0.01 \text{ mV}$  by a Leeds and Northrup potentiometer of the type K<sub>3</sub>. The reference cell used was of the type designed by Forsling, Hietanen and Sillén<sup>13</sup>. In cell(I) Beckman's glass electrodes of type 11-9080 were used; for cell(II) the bright Pt foils were cleaned with boiling HNO<sub>3</sub>, washed and ignited in an alcohol flame prior to measurement. After the addition of either a base or an acid solution both  $E_1$  and  $E_2$  attained within ten minutes a value which was found to remain constant for several hours.

#### Comparison of the glass and quinhydrone electrodes.

When two identical series of solutions were studied with a glass and a quinhydrone electrode  $E_1 - E_2$  proved to be constant within  $\pm 0.2 \text{ mV}$ . This result indicates that no appreciable complex formation occurs between Rh(III) (of concentrations studied) and quinhydrone or its dissociation products for  $\log h \geq -3$ .

### Results.

In order to calculate h and  $Z = \frac{h - H}{B}$  = average number of  $H^+$  ions set free by Rh(III) we need  $E_{O1}$  and  $E_{O2}$ . To find these quantities

$$E_1 - 59.15 \log H + E_j(H) \quad (3)$$

$$\text{and } E_2 - 59.15 \log H + E_j(H) + \delta(H) \quad (4)$$

were plotted as functions of H. When H attains such high values that the hydrolysis becomes negligible (3) and (4) will be equal to  $E_{O1}$  and  $E_{O2}$ . It was <sup>found</sup> however, that for our solutions (3) and (4) changed monotonically with H and thus up to the highest H values studied (0.120 M) appreciable amounts of hydrolysis products are present. For the low B values investigated it was of little interest to study highly acid solutions because in that region the Z values determined from emf data become rather uncertain for reasons already discussed.

Since the  $E_{O1}$  and  $E_{O2}$  values could not be determined in a straightforward manner by (3) and (4) we were forced to use successive approximation for the interpretation of the E data.

First the rough approximation was made that in each series of measurements the hydrolysis is negligible for the highest H. When  $E_O$  was calculated with this hypothesis Z was found to increase rapidly to a value of about 1.7 which seemed to remain constant until h was decreased so much that a precipitate was formed. The absorption spectra of the solution of B = 5 mM has also been measured at H = 120 and H = 4 mM. The absorption spectra in the visible range proved to be uninfluenced within the limits of experimental uncertainty by the change of acidity.

These findings led us to examine the width of the range of log h and B within which our data can be explained by assuming Z to be a constant. With this assumption we have, for the correct value of Z,

$$h = H + BZ, \quad (5)$$

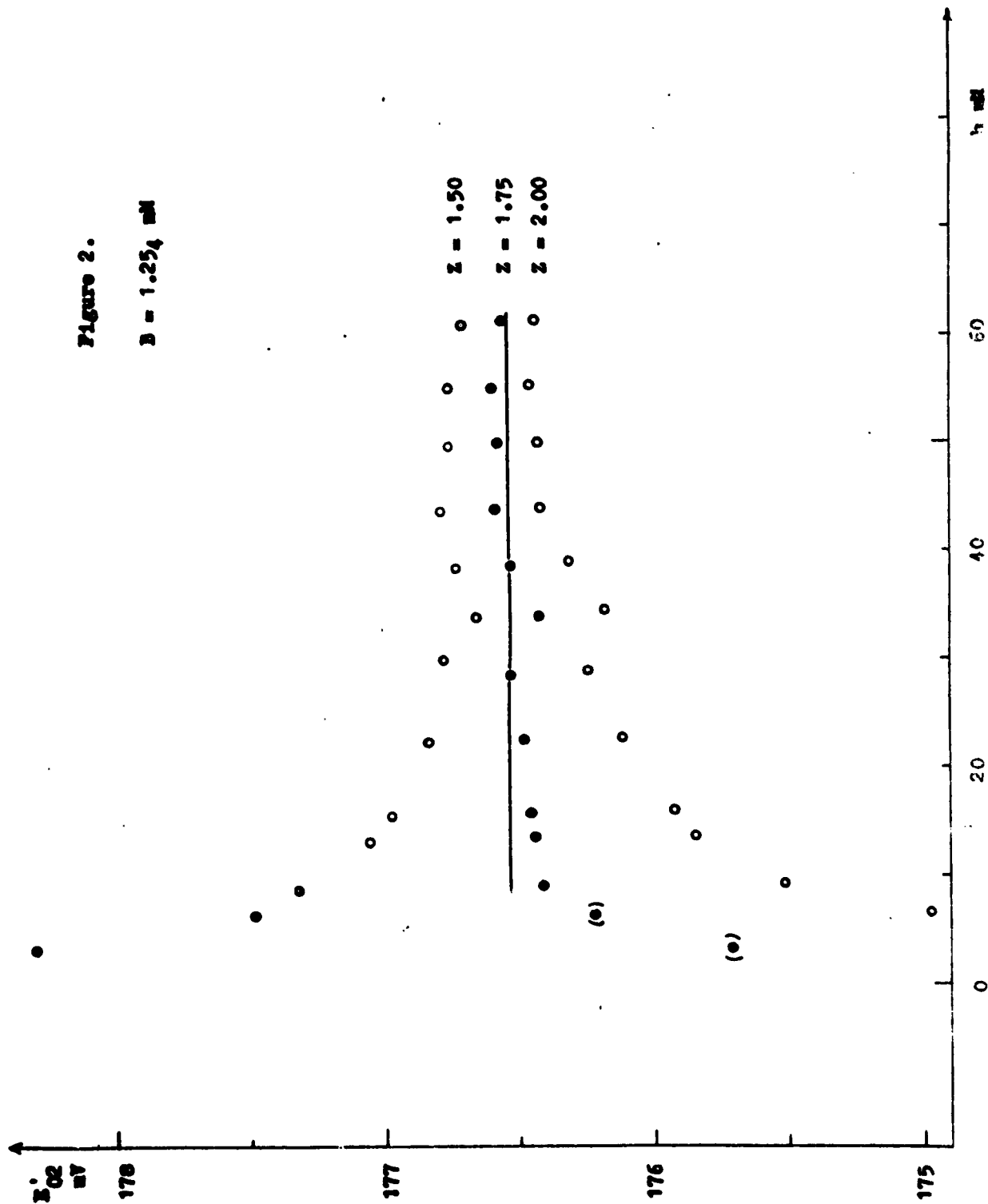
$$\text{and both } E_1 - 59.15 \log(H + BZ) + E_j(H + BZ) = E'_{O1} \quad (6)$$

$$\text{and } E_2 - 59.15 \log(H + BZ) + E_j(H + BZ) + \delta(H + BZ) = E'_{O2} \quad (7)$$

should be constants.  $E'_{O1}$  and  $E'_{O2}$  were calculated for all experimental points, assuming a series of Z values ranging from 1.50 to 2.00. (6) and (7) proved to be constant within  $\pm 0.2$  mV, calculated with Z = 1.75 whereas systematic variations were found for other Z values. Typical plots of  $E'_{O1}(H)$  and  $E'_{O2}(H)$  are shown in Figs 2, 3 and 4; the values of  $E'_{O1}$  and  $E'_{O2}$  calculated for all of the experimental points with Z = 1.75 are summarized in Table 2.

Figure 2.

$B = 1.254$  mH



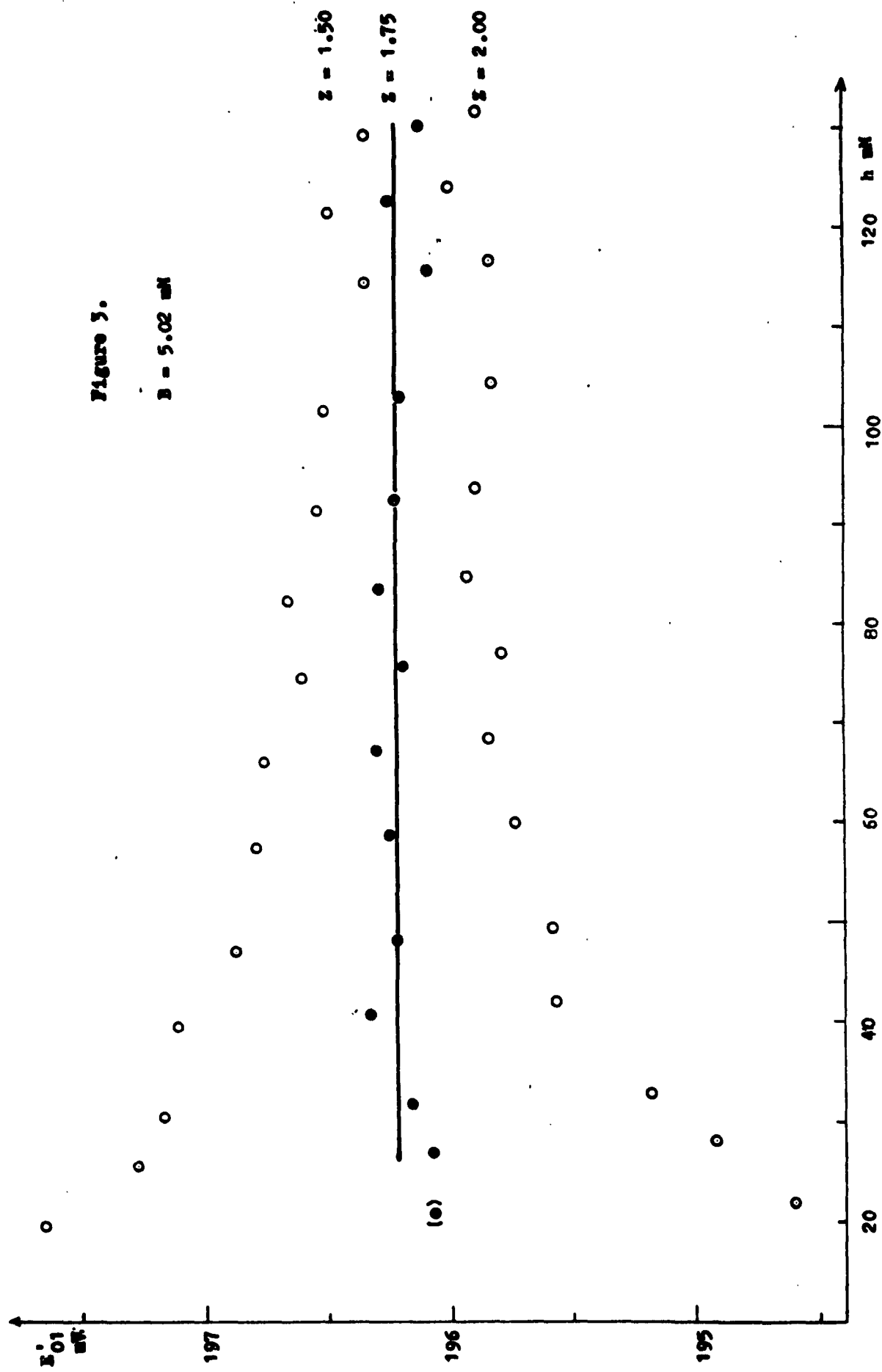


Figure 3.

$z = 5.02$  mM

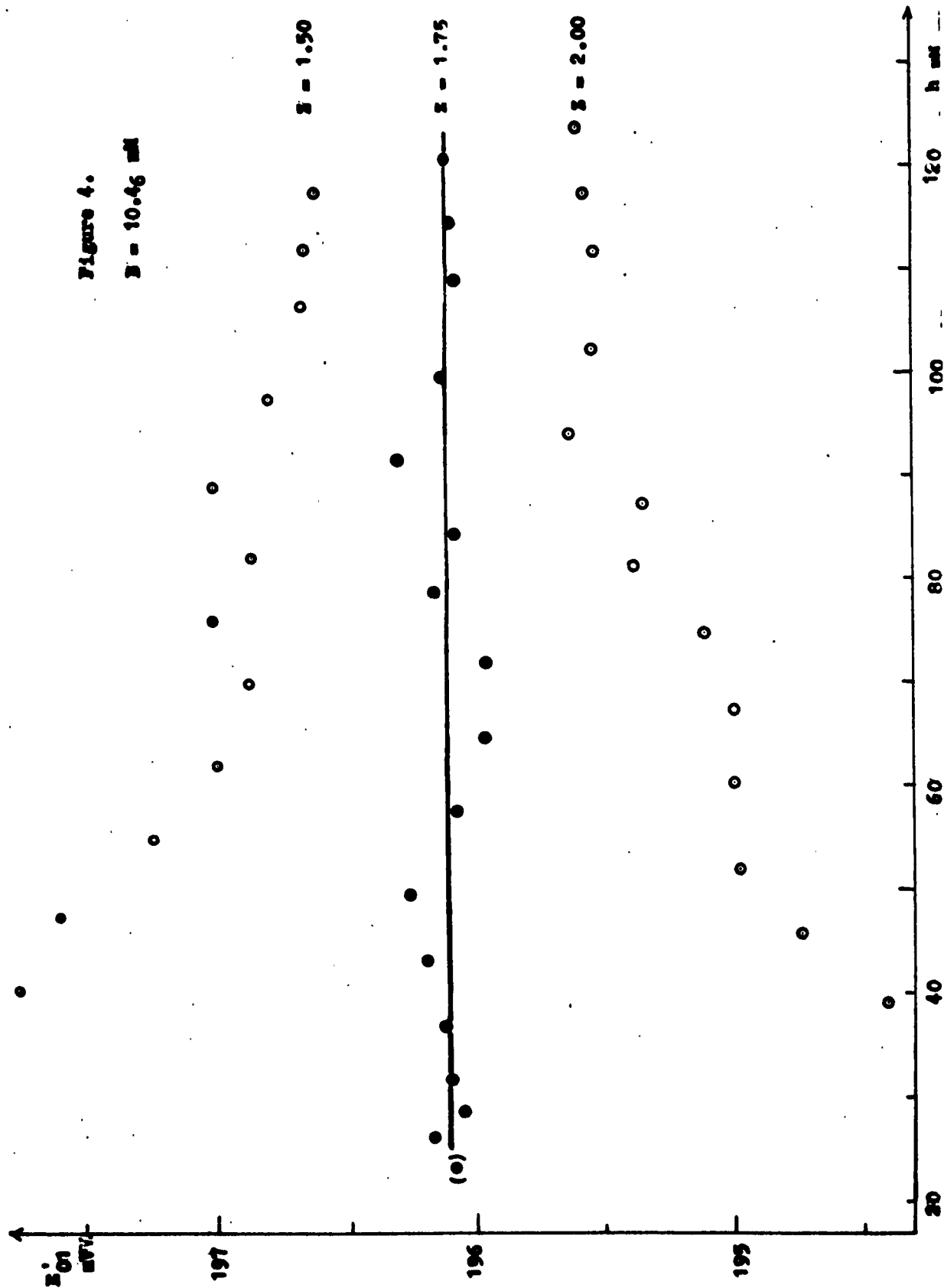


Table 2

 $B = 1.25_4 \text{ mM}$ 

H	$E_1$	h	$E'_{O1}$	H	$E_2$	h	$E'_{O2}$
mM	mV	mM	mV	mM	mV	mM	mV
58.84	302.8	61.03	198.19	58.84	281.09	61.03	176.56
55.38	301.1	57.57	197.93	52.80	278.56	54.99	176.60
52.31	299.9	54.50	198.08	47.54	276.06	49.73	176.58
46.73	297.4	48.92	198.27	41.49	272.84	43.68	176.59
42.01	295.0	44.20	198.41	36.36	269.66	38.55	176.53
37.65	292.3	39.84	198.29	31.94	266.55	34.13	176.41
32.09	288.4	34.27	198.18	26.32	262.08	28.51	176.53
26.11	283.7	28.30	198.29	20.31	256.06	22.50	176.47
20.24	277.8	22.43	198.25	13.42	245.76	15.61	176.45
15.46	271.5	17.65	198.04	11.22	242.90	13.41	176.44
11.52	265.0	13.71	197.96	6.79	232.61	8.97	176.41
8.24	258.1	10.43	198.03	(4.25	223.91	6.43	176.22)
(5.46	249.8	7.65	197.65)	(1.04	205.78	3.23	175.71)
(0.97	225.9	3.16	196.39)				

 $B = 5.02_2 \text{ mM}$ 

H	$E_1$	h	$E'_{O1}$	H	$E_1$	h	$E'_{O1}$
mM	mV	mM	mV	mM	mV	mM	mV
121.77	319.1	130.56	196.11	121.77	325.5	130.56	202.51
114.05	317.8	122.84	196.24	106.53	322.6	115.32	202.55
106.82	316.2	115.61	196.08	94.17	319.7	102.96	202.35
94.33	313.6	103.12	196.21	83.72	316.8	92.51	202.02
83.76	311.0	92.55	196.22	74.67	314.6	83.46	202.32
74.74	308.6	83.53	196.29	66.82	311.9	75.61	202.02
66.91	306.1	75.70	196.19	58.38	309.1	67.17	202.12
58.44	303.3	67.23	196.30	49.51	305.6	58.30	202.11
49.90	299.9	58.69	196.25	39.42	300.7	48.21	201.93
39.43	295.0	48.22	196.22	31.89	296.5	40.68	201.97
31.96	290.9	40.75	196.23	22.92	290.1	31.71	201.82
23.00	284.5	31.79	196.16	18.04	286.0	26.83	201.93
18.11	280.2	26.90	196.07	14.82	282.8	23.61	201.97
(12.01	273.7	20.80	196.07)	(11.94	279.2	20.73	201.66)
				( 4.11	267.1	12.90	201.62)
				(-1.77	250.0	7.02	200.05)

Table 2 (continued)

B = 5.02 <sub>2</sub> mM				B = 10.46 <sub>3</sub> mM			
H	E <sub>2</sub>	h	E' <sub>02</sub>	H	E <sub>1</sub>	h	E' <sub>01</sub>
mM	mV	mM	mV	mM	mV	mM	mV
83.71	291.38	92.50	176.62	102.34	317.2	120.65	196.10
74.52	289.14	83.32	176.92	96.35	316.0	114.66	196.08
66.83	286.86	75.62	177.00	90.81	314.8	109.12	196.06
58.32	283.98	67.11	177.05	81.36	312.7	99.67	196.12
49.82	280.64	58.61	177.04	73.21	310.8	91.52	196.29
41.49	276.79	50.28	176.99	66.34	308.7	84.65	196.07
39.38	275.76	48.17	177.02	60.36	307.0	78.67	196.15
31.89	271.52	40.68	177.01	53.91	304.7	72.22	195.95
22.92	265.15	31.71	176.88	46.39	302.0	64.70	195.95
18.04	261.02	26.83	176.97	39.40	299.3	57.71	196.06
11.94	254.46	20.73	176.93	31.18	295.65	49.49	196.23
(8.52	249.91	17.31	176.96)	24.86	292.2	43.17	196.18
				18.37	288.1	36.68	196.11
				13.44	284.4	31.75	196.09
				10.43	281.8	28.74	196.04
				7.87	279.6	26.17	196.16
				(5.01	276.6	23.32	196.08)

The values in brackets refer to solutions which probably contained some precipitate.

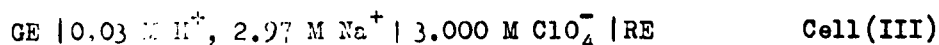
On the basis of these computations we would like to propose as the most likely explanation of our data that in the log h and B range studied Rh(III) is present as a single hydrolyzed species probably of the general composition  $(\text{Rh}(\text{OH})_{1.75 \pm 0.1})_n$ . Values of n which yield an integer for the number of OH bound to rhodium in the Z range  $1.75 \pm 0.1$  are

e.g.	n	Z	
	3	1.67	corresponding to $\text{Rh}_3(\text{OH})_5^{4+}$
	4	1.75	" $\text{Rh}_4(\text{OH})_7^{5+}$
	5	1.80	" $\text{Rh}_5(\text{OH})_9^{6+}$

On the basis of the present data we cannot give preference to any of these possibilities. Since with Z = constant all of the present data seem to be reasonably explained it cannot be decided whether one of the proposed basic units or a polymer of it exists in our solutions.

It may be of interest to mention a somewhat similar case, that of the hydrolysis of Zr(IV). Work carried out in this laboratory<sup>14</sup> gives evidence that in the log h range -3 to -0.5 Zr(IV) is present as  $(\text{ZrOOH}^+)_n$  and this single species reacts very slowly with either  $\text{H}^+$  or  $\text{OH}^-$ .

Attempts were made to give support to our conclusions that Z is a constant in the entire h range studied by determining  $E_{01}$  through measuring the emf of the cell



immediately after measurements on a Rh(III) series had been completed. The  $E_{01}$  value found with cell(III) was in some cases in excellent agreement with  $E'_{01}$  calculated by (6), (taking a Z value of 1.75) whereas in other cases deviations up to 1 mV were obtained. It is believed that the deviations are to be ascribed to a change in the surface properties of the glass electrode when this was removed from the solution, rinsed with distilled water, dried and finally put into the 0.03 M  $\text{HClO}_4$ . This type of error may be completely eliminated when the quinhydrone electrode is used.

Continued work now in progress i.e. emf and conductance measurements in a wide h and B range is expected to give a detailed picture of the hydrolysis equilibria in Rh(III) perchlorate solutions.



### Rhodium in oxidation states other than three.

#### Previous work on higher oxidation states.

The existence of Rh-ions with oxidation number higher than three was reported by several authors. (For a survey of the early work see ref. 15). The most extensive studies on the preparation and properties of rhodium ions of high oxidizing power were made by Grube and coworkers<sup>15, 16, 17</sup>. These investigations gave clear evidence that in acid solutions ( $\text{ClO}_4^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ) Rh-ions of oxidation states higher than 4 may be prepared by anodic oxidation and that they are most stable in perchlorate medium. Iodometry and potentiometric titration with Fe(II) yielded values varying between 4 and 5.8 for the oxidation state.

The difficulties encountered in connection with Grube's analyses might be explained by assuming that by anodic oxidation several reaction products might be formed (e.g.  $\text{O}_3$  and if any  $\text{Cl}^-$  was present also  $\text{Cl}_2$ ). Another reason for the spread may be the high acidity of the solutions studied. According to our experience in highly acidic solutions the rate of oxidation of  $\text{H}_2\text{O}$  by the rhodium ions of higher oxidation state becomes very rapid. It should be added that since the yield by electrolytic oxidation is rather slow, this method of preparation is somewhat inconvenient though it does not require the introduction of any foreign substances. Dwyer, Nyholm and Rogers<sup>18</sup> in 1947 have prepared the slightly soluble salt  $\text{Cs}_2\text{RhCl}_6$  that contains Rh(IV). On the basis of this result Dwyer and Schafer<sup>19</sup> have claimed that by anodic oxidation of a strongly acid  $\text{Rh}_2(\text{SO}_4)_3$  solution Rh(IV) is formed.

It has been known for a long time that Rh(III) could be oxidized by  $\text{OCl}^-$  or  $\text{OBr}^-$ . This reaction has been used in separation processes and it forms the basis of a colorimetric determination of rhodium<sup>20</sup>. Ayres, in connection with his colorimetric studies<sup>21</sup> reported some attempts to determine the oxidation state of a purple-colored Rh-species obtained by hypochlorite oxidation. The Rh-ions were separated by cation exchanger from the excess hypochlorite and the oxidizing power of the eluate was determined iodometrically. Ayres found for the oxidation number values varying from 4 to about 5.3.

Syrokonskiĭ and Proshenkova<sup>22</sup> were able to oxidize very dilute Rh(III) solutions containing sulfuric (and probably some hydrochloric acid) by adding a large excess of  $\text{NaBiO}_3$ . The oxidation state of the blue-violet ion formed was determined by titration with Fe(II). Their results (with an accuracy of  $\pm 5\%$ ) indicate that the rhodium present in the solution had an oxidation number of 5.

### Oxidation of Rh(III) by means of ozone.

We have found that rhodium ions of higher oxidation state can rapidly be prepared by means of ozone,  $O_3$ . The rate of oxidation is influenced mainly by the total concentration of rhodium and by the acidity. It seems to be most convenient to carry out the oxidation at  $pH \sim 8$  (e.g. in borax buffer solution). At this pH, solutions of Rh as dilute as 0.2 mM may be oxidized quantitatively to Rh(V) within half an hour.

Ozone is certainly to be preferred to other oxidizing agents since no foreign substances are introduced into the solution and the excess of  $O_3$  is easily removed e.g. by passing  $N_2$  through.

### Oxidation number of the higher valency.

We made some preliminary experiments to determine the oxidation number of the green ions formed by ozonization. In an acid solution ( $ClO_4^-$ ,  $SO_4^{2-}$ ) of known  $[Rh(III)]$  and of measured volume the pH was adjusted with dilute NaOH and borax to about 8 (measured by indicator paper). Ozone was then passed through the solution at  $0^\circ C$  for half an hour. The solution became rapidly dark green, and some of the Rh formed a greenish black precipitate. Prolonging the period of ozonization did not increase the oxidizing power of the solution. After the ozonization had been completed nitrogen was bubbled through the solution for 5-10 minutes to remove the ozone and the oxygen. A  $CO_2$  atmosphere was established,  $HClO_4$  or  $H_2SO_4$  was added, which dissolved the precipitate and raised the  $[H^+]$  to a value between 10 - 100 mM. At this stage NaI was added and the liberated  $I_2$  was titrated with a standardized solution of  $Na_2S_2O_3$ .

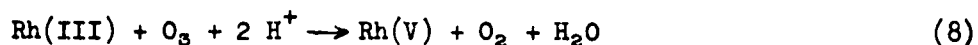
The results of these experiments are shown in the Table 3 which indicates that Rh(V) is formed by the reaction of ozone with Rh(III) under these experimental conditions.

Table 3

Medium	Rh(III) mol $10^6$	$2(I_2 \text{ found})$ mol $10^6$	change of oxidation number: $2 I_2 / Rh(III)$
$SO_4^{2-}$	5.87	10.48	1.79
	5.87	13.08	2.22
	5.87	11.42	1.94
	5.87	11.27	1.92
	14.69	31.80	2.16
$ClO_4^-$	8.34	17.03	2.04
	8.34	17.54	2.10

These determinations should be regarded only as preliminary ones, it is believed that the spread is due to a small  $\text{Cl}^-$  content of the solutions used. Attempts to determine the oxidation state of the green species by reducing it to the metal state with  $\text{N}_2\text{H}_4$  solution have been unsuccessful. The excess of  $\text{N}_2\text{H}_4$  was found to be decomposed in the presence of finely divided rhodium metal. Fig. 5 shows the absorption spectrum of the  $\text{Rh(V)}$  species where that of  $\text{Rh(III)}$  is also given for comparison.

To study the properties of the  $\text{Rh(V)}$  ion is of considerable interest for analytical and preparative purposes. The reactions:



may form the basis of a convenient and accurate volumetric method of determining rhodium and this might replace the gravimetric processes which require a relatively large amount even of moderately concentrated  $\text{Rh}$ -solutions (100 mg  $\text{Rh}$  = 100 ml of 10 mM  $\text{Rh}$ -soln.). Work is now being carried out with rhodium solutions of widely varying concentration to find the most suitable experimental conditions for reactions (8) and (9).

The importance of reaction (8) in connection with the preparation of rhodium perchlorate solutions is discussed in the Appendix.

#### Other oxidizing agents.

Some other oxidizing agents were also tried. With  $\text{Ce(IV)}$  and  $\text{Ag(II)}$  only partial oxidation could be achieved. Slight oxidation could be observed with  $\text{S}_2\text{O}_8^{2-}$  in hot solution but  $\text{Rh(V)}$  is decomposed rapidly at higher temperatures. The oxidation could be made quantitative with  $\text{IO}_4^-$  but the reaction is complicated by complex formation between  $\text{Rh(V?)}$  and  $\text{IO}_4^-$  which must be added in great excess. A study is now being made in this laboratory to develop a colorimetric method based on the reaction between  $\text{Rh(III)}$  and  $\text{IO}_4^-$ , which may be used for the determination of 0.1 - 1.0 mg quantities of  $\text{Rh}$ .

#### Reduction of $\text{Rh(III)}$ by $\text{H}_2$ or formic acid.

A few experiments were also made to prepare rhodium ions of oxidation state lower than three. When  $\text{Rh(III)}$  is being reduced by  $\text{H}_2$ , the original yellow color of the solution changes to green and simultaneously finely divided  $\text{Rh}$  metal is formed (cf. chapter on the analysis of  $\text{Rh}$ -solutions).

If the metal powder is removed from the solution by centrifuging the green color slowly changes to yellow. The finely divided rhodium prepared by  $H_2$  is - in contrast to the compact metal - fairly reactive, it can e.g. be dissolved in 1 M  $HClO_4$ . It is believed that the green ions are formed by a reaction between  $Rh(III)$  and the rhodium powder.

On heating with sodium formate  $Rh(III)$  was reduced and the color of the solution became turquoise. When the rhodium metal had been separated by centrifuging the clear solution obtained did not change its color for many days. This solution, when acidified, proved to have strong reducing properties: on adding  $MnO_4^-$ ,  $Mn(II)$  and  $Rh(III)$  were formed;  $Ag^+$  was reduced to metal, and  $Hg^{2+}$  to  $Hg_2^{2+}$ . (Acidification was necessary before these experiments were made in order to avoid reduction by the formate ions present in excess.) The absorption spectrum of this greenish-blue solution shown in Fig. 7 is distinctly different from that of the  $Rh(III)$  and  $Rh(V)$  species. (cf. chapter Extinction curves.)

Further studies are planned to determine the oxidation number of the  $Rh$ -species formed by  $H_2$  and by the formate ion.

### Extinction curves.

#### Spectra of $Rh(III)$ species

The measurements with  $Rh(III)$  solutions were started to find out if small amounts of chloride could be conveniently detected by absorption spectra. It was especially interesting to study the visible region because in that interval the extinction coefficients containing  $Rh(III)$  in the concentration range 1 to ~20 mM are rather low, consequently no need arises, as in the ultraviolet region, to use cells of length less than 0.5 cm which are difficult to manipulate.

The absorption spectra of a series of rhodium(III) chloride, sulfate and perchlorate solutions of various acidities have been studied in the wavelength interval 200 - 1000 m $\mu$  (2000 - 10000 Å). The data summarized in Fig. 6 and in Table 4 were obtained with a Hilger model UVISPEK spectrophotometer which was placed in a thermostated room at  $25.0 \pm 0.5^\circ C$ ; the wavelength scale of the apparatus had recently been calibrated. Silica cells (of optical paths 0.10 to 4.00 cm) were used.

At wavelengths lower than ~220 m $\mu$  the reliability of the measurements decreases rapidly with increasing frequencies. The presence of

oxygen and the imperfections of the apparatus (e.g. diffraction on irregular optical surfaces) might have caused considerable systematic errors.

As it may be inferred from Fig. 6, the spectra of the different rhodium(III) species do not differ so much in the visible region that small amounts of chloride could be detected either in the sulfate or in the perchlorate solutions with the apparatus used.

The absorption maxima and minima characteristic for the rhodium(III) solutions studied are summarized below in

Table 4.

Solution	$\lambda_{\max}$ m $\mu$	$\epsilon_{\max}$ gmole $^{-1}$ cm $^2$	$\lambda_{\min}$ m $\mu$	$\epsilon_{\min}$ gmole $^{-1}$ cm $^2$	$\lambda_i$ m $\mu$	$\epsilon_i$ gmole $^{-1}$ cm $^2$
Rh(III)- chloride	475 $\pm$ 2 (205)	85.5 (16900)	440 $\pm$ 2	77.5	370 (220 $\pm$ 2)	237 (15700)
Rh(III)- perchlorate	(195 $\pm$ 1)	(8300)			400 230-250	174 2560
Rh(III)- sulfate	404-408 (192 $\pm$ 1)	98.3 (8900)	373-377	90.1		

i denotes the point of inflection

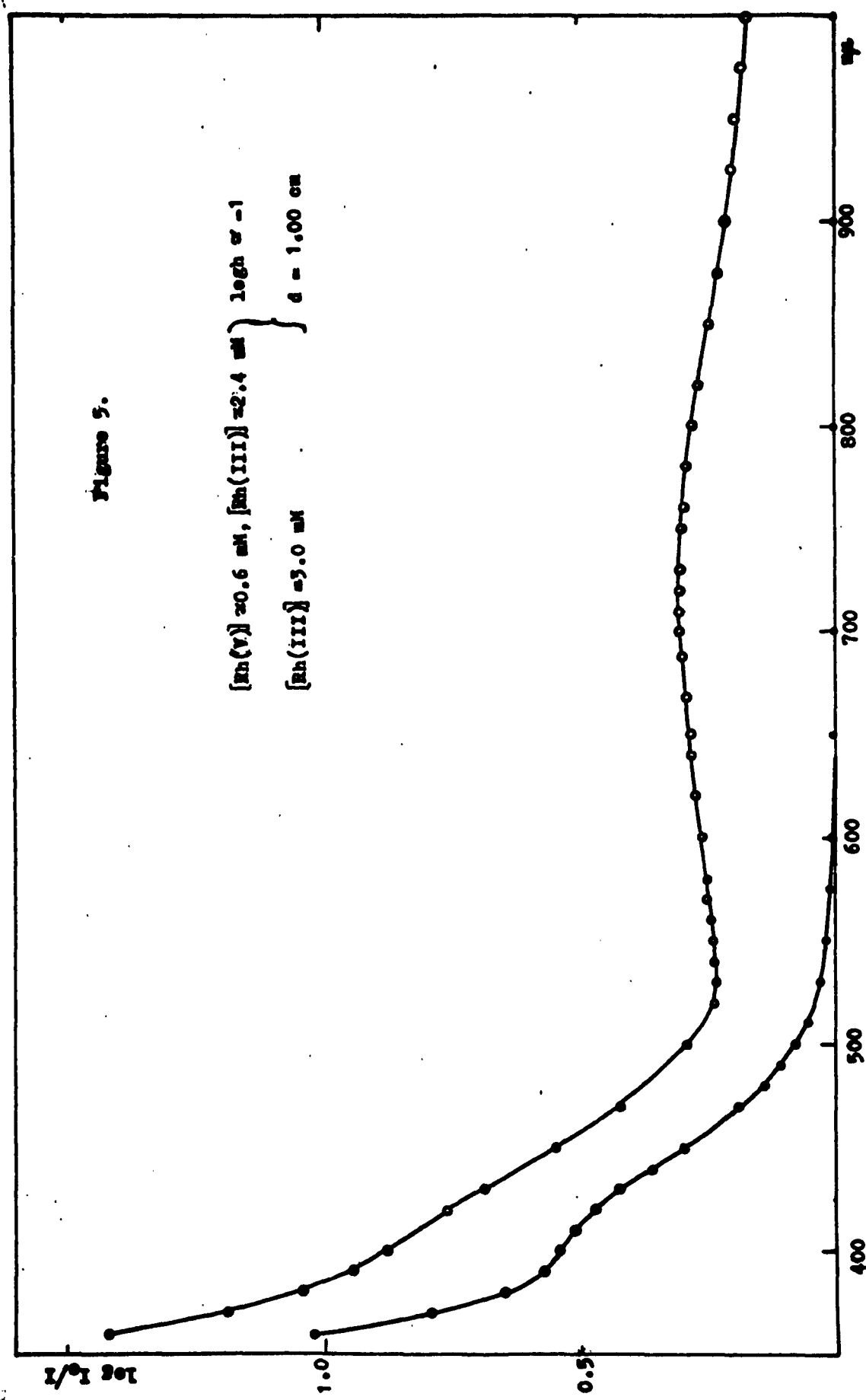
It has already been discussed in a previous section (see page 1:8) that it is not worthwhile to attempt to explain the spectra before the composition of the species present at different acidities and [Rh(III)] have been ascertained by emf and conductance measurements.

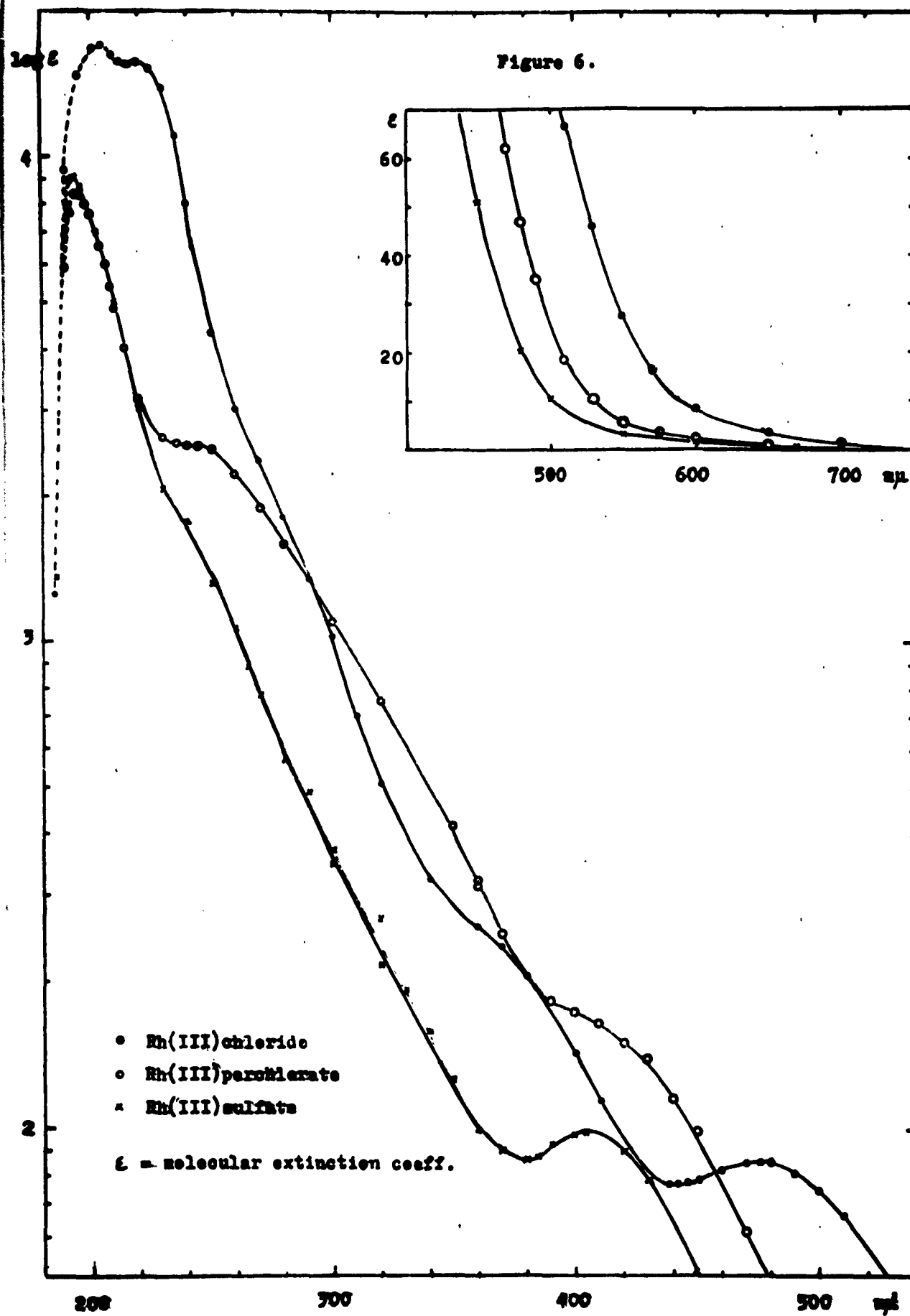
#### Spectra of the Rh(V) species.

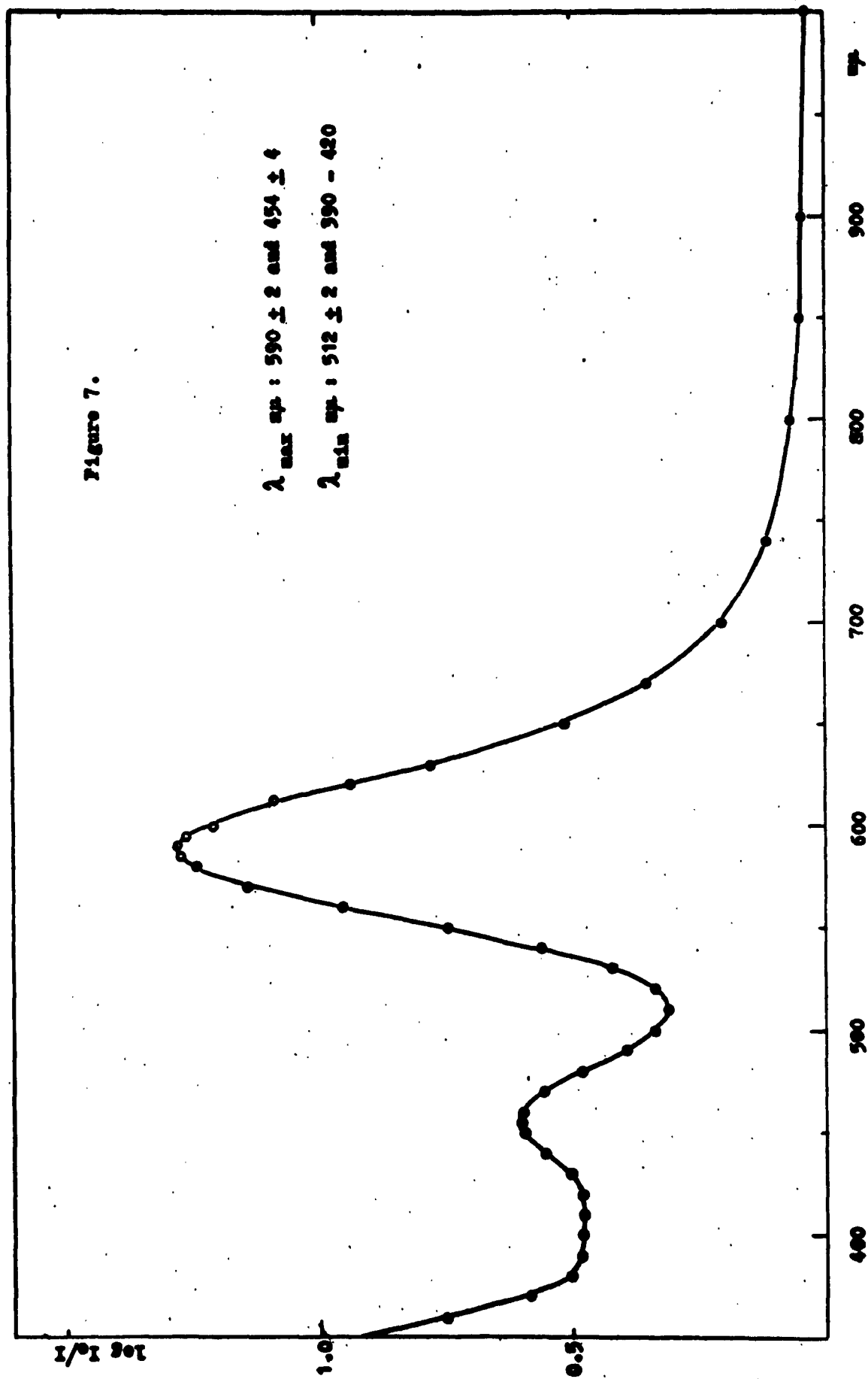
The absorption spectrum of rhodium(V) perchlorate solution is shown in Fig. 5. Essentially the same absorption curve is obtained in sulfate medium. The difference between the spectra of Rh(III) and Rh(V) is so pronounced that small amounts of one species can easily be recognized in the presence of a great excess of the other one. As a consequence the rate of oxidation of water by Rh(V) could be conveniently studied by measuring the change in the absorption spectra.

#### Spectra of a Rh-species in a lower oxidation state.

The absorption spectra (360 - 1000 m $\mu$ ) of the species formed by reduction of Rh(III) with formic acid (see page 1:16) is shown in Fig. 7. The striking difference between the spectrum of the reduced form and that of either Rh(III) or Rh(V) suggests that the reduced form has a characteristic electron structure.









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MONITORING AGENCY DOCUMENT NO.  
ASTIA DOCUMENT NO.

Notes on the preparation and analysis of halogenide-free  
rhodium(III) perchlorate (sulfate) solutions

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TECHNICAL NOTE NO. 2

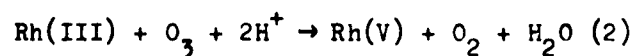
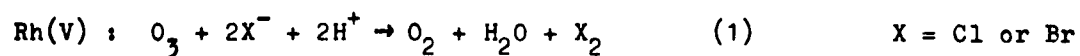
CONTRACT NO. AF 61(052)-181

DATE OF REPORT: Febr 15, 1960

The research reported in this document has been sponsored by the AIR FORCE  
CAMBRIDGE RESEARCH CENTER of the AIR RESEARCH AND DEVELOPMENT COMMAND, UNITED  
STATES AIR FORCE, through its European Office.

### Abstract

A method is described for the preparation of halogenide-free rhodium(III) perchlorate (sulfate) solutions. As starting material, rhodium chloride or rhodium bromide can be used. The halogenide was removed by means of ozone, which oxidizes "free" (not complex-bound) halogenide to halogen and Rh(III) to



The Rh(V) produced, being a strong oxidizing agent, also reacts with the halogenide according to  $\text{Rh(V)} + 2\text{X}^- \rightarrow \text{Rh(III)} + \text{X}_2$  (3)

Methods for the detection of halogenide-ions in rhodium solutions are given.

Notes on the preparation and analysis of halogenide-free rhodium(III)  
perchlorate (sulfate) solutions.

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Problem

For studies on the hydrolysis and other reactions of rhodium(III) and rhodium-ions of higher oxidation states, it was desired to prepare rhodium(III) perchlorate and sulfate solutions that were free from detectable amounts of halogen ions. As is well known, the halides<sup>1</sup> form strong complexes with rhodium(III) and also with rhodium of higher oxidation states. Moreover, it is known<sup>2,3</sup>, and was confirmed in the present work, that the formation and breakdown of the halogeno rhodium complexes is a rather slow process. Hence, in a solution containing appreciable amounts of halogenide, one may expect a very slow establishment of also other equilibria.

In preliminary experiments, methods proposed by previous authors<sup>4a,4b,5,6,7a,7b</sup> proved to give unsatisfactory results - in general, the solutions still contained halogenide (for analysis methods, see end of report). Moreover, none of these methods seems to be practical for the preparation of a substantial amount of relatively concentrated perchlorate solution.

It has, however, proved possible to develop a new method which seems to give rhodium solutions that are sufficiently free from halogenide ions and therefore suitable as a starting material for studies concerning this element.

Starting material: chloride or bromide

As starting material in all the initial experiments, solid  $\text{RhCl}_3(\text{H}_2\text{O})_4$  of a purity higher than 99.7 % (delivered by A.D. MacKay, Inc.) was used.

Alkali or sulfate ions could not be detected in the preparation.

Later on, a rhodium bromide solution (stoichiometric composition undetermined) was found to be a still more convenient starting material.

$\text{RhBr}_3(\text{H}_2\text{O})$  was first prepared from its components by Goloubkin in 1910<sup>8a,8b</sup>. Spongy Rh (1 g) was sealed in a tube with 24 g 40 % HBr and 7 g and kept  $\text{Br}_2$  at 80-100°C for 48 h. We found, however, that a simpler procedure gave equally good results: finely divided rhodium metal was found to dissolve in the mixture of HBr +  $\text{Br}_2$  if it was refluxed on a water bath for 24 h. After the metal had dissolved, the excess of reagents was distilled off under reduced pressure. The dry residue was redissolved in water and once more evaporated to dryness. The substance obtained had a deep brown color with a tinge of violet and was completely soluble in water.

This method of synthesis is very convenient and we now feel that rhodium bromide prepared in this way is preferable to rhodium chloride as the first step in the preparation of rhodium solutions. The method has the added advantage that one can use rhodium metal residues from the classical gravimetric rhodium determination according to Gilchrist and Wichers (sulfide → oxide → reduction in  $\text{H}_2$  atmosphere at about 450°C) and also rhodium recovered from various waste solutions by reduction with hydrazine or hydrogen, washing, igniting and reducing it again.

Preparation of perchlorate (sulfate) from halogenide: experience with older methods

Rhodium does not dissolve directly in  $\text{HClO}_4$ . On the other hand, the metal may be brought slowly into solution by boiling with a large excess of conc. sulfuric acid or by fusion with potassium pyrosulfate ( $\text{K}_2\text{S}_2\text{O}_7$ ). These methods of dissolution have - for our purposes - a theoretical interest only. They require the introduction of an immense excess of the reagent which cannot be easily removed.

Thus, in order to prepare a rhodium perchlorate (sulfate) solution, it is necessary to start with a soluble salt.

The following methods employing  $\text{RhCl}_3(\text{H}_2\text{O})_4$  may be found in the literature.

1. According to Grube<sup>4a,4b</sup>, the rhodium(III) hydroxide can be precipitated, washed, and dissolved in  $\text{HClO}_4(\text{H}_2\text{SO}_4)$ , under suitable conditions.
2. Recently, Shukla<sup>7a,7b</sup> proposed removing the chloride by adding  $\text{AgClO}_4$ .
3. Jørgensen<sup>5</sup>, and Ayres and Forrester<sup>6</sup> recommended evaporation with excess  $\text{HClO}_4(\text{H}_2\text{SO}_4)$ .

In addition, one might suggest

4. Passing a rhodium(III) chloride solution through a  $\text{ClO}_4^-$  or  $\text{SO}_4^{2-}$ -saturated anion exchanger.

Attempts were made to use Grube's method but it was soon found that the resulting solutions always contained considerable amounts of chloride. Since the final  $\text{Cl}^-$  content is much influenced by the experimental conditions chosen, the procedure will be briefly described. A dilute solution of  $\text{RhCl}_3(\text{H}_2\text{O})_4$  (2 g/l) in distilled water was prepared, filtered, and then kept nearly boiling for at least one hour in order to destroy, as far as possible, the chloro-rhodium complexes. To the hot solution, strong  $\text{NaOH}$  was added till the pH was around 9 (as measured by spot test on an indicator paper). By that time, some of the rhodium had again dissolved as hydroxo complexes. The acidity was then adjusted with  $\text{HClO}_4$  until all rhodium was precipitated as rhodium(III) hydroxide.

The rhodium(III) hydroxide may also be precipitated using  $\text{Na}_2\text{CO}_3$  solution, the solution being first made alkaline to pH 9. The precipitation seems to be complete after acidification to  $\text{pH} \sim 7^3$ . The pH of the colorless supernatant liquid was between 5.7 and 6.

The precipitate was repeatedly centrifuged and washed until no  $\text{Cl}^-$  could be detected in the washings. Finally, it was dissolved in cold conc.  $\text{HClO}_4$  or conc.  $\text{H}_2\text{SO}_4$ .

It was found, however, that the resulting solutions were not free from  $\text{Cl}^-$ . Even if the procedure was carried out twice, there remained about 0.16  $\text{Cl}^-$  per Rh. It is believed that the  $\text{Cl}^-$  is retained in the precipitate, perhaps in the form of a hydroxide-chloride. This agrees with the fact that previous investigators also found some evidence for the formation of rhodium(III) hydroxide chloride<sup>10</sup> and hydroxide bromide<sup>8a,8b</sup> under similar experimental conditions.

Preliminary experience with methods 2,3 and 4 indicated that they were not well suited for the preparation of a substantial amount of relatively concentrated rhodium perchlorate (sulfate) solution. Moreover, none of the methods gave a product free from  $\text{Cl}^-$ . Details about our experience with methods 2,3 and 4 will be given in a following technical note.

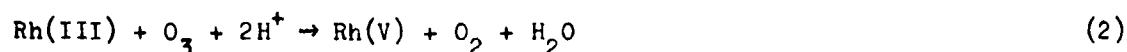
Since none of the methods, nor the anion exchange method, gave satisfactory results, it was considered best to develop a new method. The greatest difficulty seems to be the stability of the halogeno rhodium complexes - only those methods could be considered which do not involve the introduction of substances that are undesirable and hard to remove.

#### The ozone method

The method presented here is based on preliminary experiments made by this author with the intention of devising a procedure for transforming rhodium(III) into higher oxidation states by means of ozone,  $\text{O}_3$ . The reaction of ozone with solutions of rhodium and other platinum metals will be the subject of a forthcoming publication.

Whenever "chloride" is mentioned in the following, the statements are equally true for bromide. In a preliminary experiment, solid  $\text{RhCl}_3(\text{H}_2\text{O})_4$  was dissolved in water ( $[\text{Rh}] \sim 10 \text{ mM}$ ,  $[\text{H}^+] \sim 10 \text{ mM}$ ). The solution was cooled to  $0^\circ\text{C}$  and ozone passed through it. Only negligible amounts of chlorine were evolved. It was found however that, if the solution had been boiled for a while before ozonizing, chlorine was then given off much faster and moreover rhodium(III),

which is orange-yellow, was partly oxidized to a green species. Studies in progress gave evidence that this species is rhodium(V), so the reactions are:



Yeatts and Taube<sup>11</sup> recently studied the kinetics of reaction (1). They found that the rate of oxidation is considerable at 0°C but that it is much slower than the oxidation of bromide<sup>12</sup>. In the following, all experiments were carried out on solutions that had been kept nearly boiling for at least one hour in order to break up the chloro complexes.

When solutions of Rh with concentrations between 0.05 and 0.3 M and  $[\text{H}^+] \geq 0.2$  M were ozonized, chlorine was evolved for a while at a continually diminishing rate. The solution rapidly turned green because of reaction (2). When no  $\text{Cl}_2$  could be detected in the outflowing gas (absorption in NaOH, acidifying and adding  $\text{Ag}^+$ ), the solution was again put on the water bath. Chlorine was again given off, presumably because of the reaction:



The solution slowly turned greenish-brown due to the Rh(III). When the formation of  $\text{Cl}_2$  had ceased, the solution was again cooled and ozonized at 0°C - once again, a strong evolution of  $\text{Cl}_2$  was observed.

These experiments indicate that the oxidation of free  $\text{Cl}^-$  is rapid whereas the rate of reaction between ozone and  $\text{Cl}^-$  bound in Rh complexes is practically negligible.

It is possible to remove all the chloride from a rhodium chloride solution by alternately heating and ozonizing in the cold. This process is, however, rather time-consuming because, under these experimental conditions, the rate of dissociation of the complexes and the oxidation of Rh(III) are rather slow.

It was found that, by lowering the acidity, one could increase the rate of reaction (2) considerably. It seems that, at lower pH values, reaction (2) reaches an equilibrium state when only a part of the Rh has been transformed



to Rh(V). At low acidities, a larger fraction of Rh(V) is obtained and it seems that the redox potential of the Rh(V)/Rh(III) couple is increased so that reaction (3) - especially at higher temperature - gives a higher yield. It should be added that Rh(V) presumably forms weaker chloro complexes than Rh(III).

In developing a final procedure for removing  $\text{Cl}^-$  with the ozone method, it is necessary to make certain that the chloro complexes are broken up as much as possible. This is favored by 1) dilution, 2) increasing the temperature, 3) decreasing the acidity, 4) oxidizing Rh(III) to Rh(V). It is, of course, also important for the following equilibrium studies that no other foreign substance, except for some  $\text{Na}^+$  and the anion desired, is introduced into the final solution.

#### Method of preparation

Rhodium chloride is dissolved in distilled water to a concentration of about 10 mM. The solution is kept at 90-100°C for 1 h and then 5 M NaOH is added until a pH ~ 8 to 9 is attained. At this pH, the rhodium is partly present as a soluble hydroxo complex. Then, concentrated perchloric acid (or conc. sulfuric acid) is added dropwise until the pH is about 5.7 to 6. At this value, the rhodium is practically completely precipitated.

The precipitate is decanted, centrifuged, washed with hot water and centrifuged again, after which it is dissolved in a minimum of cool concentrated  $\text{HClO}_4$  or  $\text{H}_2\text{SO}_4$ . In this first step, about 90 % of the  $\text{Cl}^-$  is removed.

The solution is diluted to  $[\text{Rh}] \sim 10$  mM, kept on a water bath for 1 h and then ozonized at 0°C and pH ~ 1. When the evolution of  $\text{Cl}_2$  has practically ceased, NaOH is added to the solution (still in the ozonizing apparatus) until the pH is 5 or 6. The color then changes very rapidly to dark green due to rhodium(V).

The solution is now acidified to pH 1 or 2 and kept almost boiling: chlorine is evolved vigorously. The solution is then tested for  $\text{Cl}^-$  (see below). The ozonization at pH 6 and 0°C and the heating at pH 1 are repeated until the

test becomes negative. When the product is satisfactory (usually two cycles suffice), the rhodium(III or V) is precipitated as hydroxide as before, dissolved in the desired amount of conc. acid and, finally, the rhodium(V) is reduced with  $\text{H}_2\text{O}_2$ .

The method was first worked out for chloride, on which most experiments have been made. It has been found, however, that bromide is preferable since the reaction (3) is much more rapid with  $\text{Br}^-$  than with  $\text{Cl}^-$ .

#### Detection of halogenide ions

The common test for  $\text{Cl}^-$  using  $\text{Ag}^+$  is not reliable in solutions containing rhodium since the main part of the  $\text{Cl}^-$  is bound to Rh as complex species and does not react with  $\text{Ag}^+$ .<sup>2</sup> Moreover, in dilute solutions that do not contain any halogenide, a light pink precipitate had been observed which contains both Ag and Rh.

In sulfate solutions, the test for halogenide is very simple. Rhodium can be reduced to the metallic state from an acid solution if  $\text{H}_2$  is bubbled through at 60-70°C in the presence of a Pt-foil or wire which seems to catalyze the reduction. After the metal has been separated by centrifuging, the halogenide can of course be detected with  $\text{Ag}^+$ .

In the presence of perchlorate ions, this method is no longer reliable since some  $\text{ClO}_4^-$  is reduced to  $\text{Cl}^-$ , probably due to the catalyzing influence of the finely divided Rh(s). Nor was it practical to remove Rh by reduction to metal with hydrazine in alkaline solution since, in this case, some  $\text{ClO}_4^-$  was also reduced to  $\text{Cl}^-$ .

With perchlorate solutions, it seemed unavoidable to precipitate rhodium(III or III + V) hydroxide with NaOH, to separate the precipitate by centrifuging and to test both the precipitate and the supernatant liquid (which is free from Rh) for  $\text{Cl}^-$ . It is necessary to be rather careful with the pH. If the pH is adjusted to about 5.7 after the precipitation, then the

formation of colloidal rhodium(III) hydroxide, which makes the detection of AgCl difficult, ~~seems~~ to be avoided. Heating is also helpful for coagulating the colloid.

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ASTIA NO.

Contract No: AF 61(052)-181

United States Air Force, Air Research and Development  
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by Clara Berecki-Biedermann

February 15, 1960

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by means of ozone, which oxidizes "free" (not complex-bound) halogenide to halogen and Rh(III) to Rh(V):

$$\text{O}_3 + 2\text{X}^- + 2\text{H}^+ \rightarrow \text{O}_2 + \text{H}_2\text{O} + \text{X}_2 \quad (1) \quad \text{X} = \text{Cl or Br}$$

$$\text{Rh(III)} + \text{O}_3 + 2\text{H}^+ \rightarrow \text{Rh(V)} + \text{O}_2 + \text{H}_2\text{O} \quad (2)$$

The Rh(V) produced, being a strong oxidizing agent, also reacts with the halogenide according to

$$\text{Rh(V)} + 2\text{X}^- \rightarrow \text{Rh(III)} + \text{X}_2 \quad (3)$$

Methods for the detection of halogenide-ions in rhodium solutions are given.

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## Studies on ruthenium chemistry

By Felipe Brito

### Introduction

The primary aim of the investigations to be described is to study the hydrolysis of ruthenium(III) and ruthenium(IV) by means of the general methods that have been developed in this laboratory. As a preliminary, it proved necessary to test the methods for preparation and analysis of Ru(III) and Ru(IV) solutions described in literature, and also to work out new methods that seem more precise.

We tried first to use a perchlorate medium which has been used in most other studies in this department and has the advantage that, usually, the complex formation with the medium ions is a minimum. Amber-red solutions of ruthenium(IV) in  $\text{HClO}_4$  could be obtained by reducing  $\text{RuO}_4$  with  $\text{H}_2\text{O}_2$  and boiling off the excess of  $\text{H}_2\text{O}_2$ . However, it was found that these solutions precipitate  $\text{RuO}_2(\text{H}_2\text{O})_x$  on standing. For instance, in a filtered solution with  $\text{H}^+$  as high as 150 mM, the total concentration, B, of Ru(IV) was finally less than 2 mM; in such a solution, H would be too high and B too low for our purpose. Moreover, solutions of ruthenium(III) in perchloric acid, obtained by electrolytic reduction of a ruthenium(IV) perchlorate solution, proved to be unstable, Ru(IV) and  $\text{Cl}^-$  being formed; this agrees with the findings of Wehner and Hindman<sup>1</sup>.

For our purposes, it was desirable to have solutions with a low analytical  $\text{H}^+$  concentration (H) and a large total concentration (B) of that oxidation state of Ru whose hydrolysis was to be studied. The reaction might be followed by measuring either the free concentration of  $\text{H}^+$  (h) with a glass electrode, or the remaining free concentration of  $\text{Ru}^{3+}$  or  $\text{Ru}^{4+}$  (b) using, for instance a redox electrode.

Since there were disadvantages with other media, such as those containing chloride, it was decided to use a sulfate medium despite certain difficulties, particularly the formation of  $\text{HSO}_4^-$  and the possibility of rather strong complexing.

Later on, however, we found a method for preparing solutions of Ru(IV) in perchlorate medium and with suitable values for B and H. So, it was decided, first, to study the hydrolysis of Ru(IV) in 3 M  $(\text{Na})\text{ClO}_4$  medium with glass electrodes, and then the hydrolysis of Ru(III) and Ru(IV) in  $(\text{Na}_2)\text{SO}_4$  medium, using both glass and redox electrodes.

The results obtained through May, 1960, are given in the following. As will be seen, there have been many experimental difficulties. However, we hope that our limited experience will prove of some use to others.

Preparation of ruthenium(III) and ruthenium(IV) in sulfate medium.

Preparation and spectra (scheme I and fig2. For clarity, the various solutions obtained will be denoted by letters: S, G<sub>1</sub>, B<sub>1</sub>, etc). The starting material was commercial ruthenium chloride (40 % Ru) from which a chloride-free ruthenium sulfate solution was prepared by repeated evaporation in 25% sulfuric acid under an infrared lamp during which SO<sub>3</sub> fumes appeared - this ensured the removal of Cl<sup>-</sup> and Os<sup>1</sup>. From this solution, RuO<sub>4</sub> was prepared by oxidation with KMnO<sub>4</sub><sup>2,3,4,6</sup>. Each of the experiments to be described has been repeated several times with various modifications.

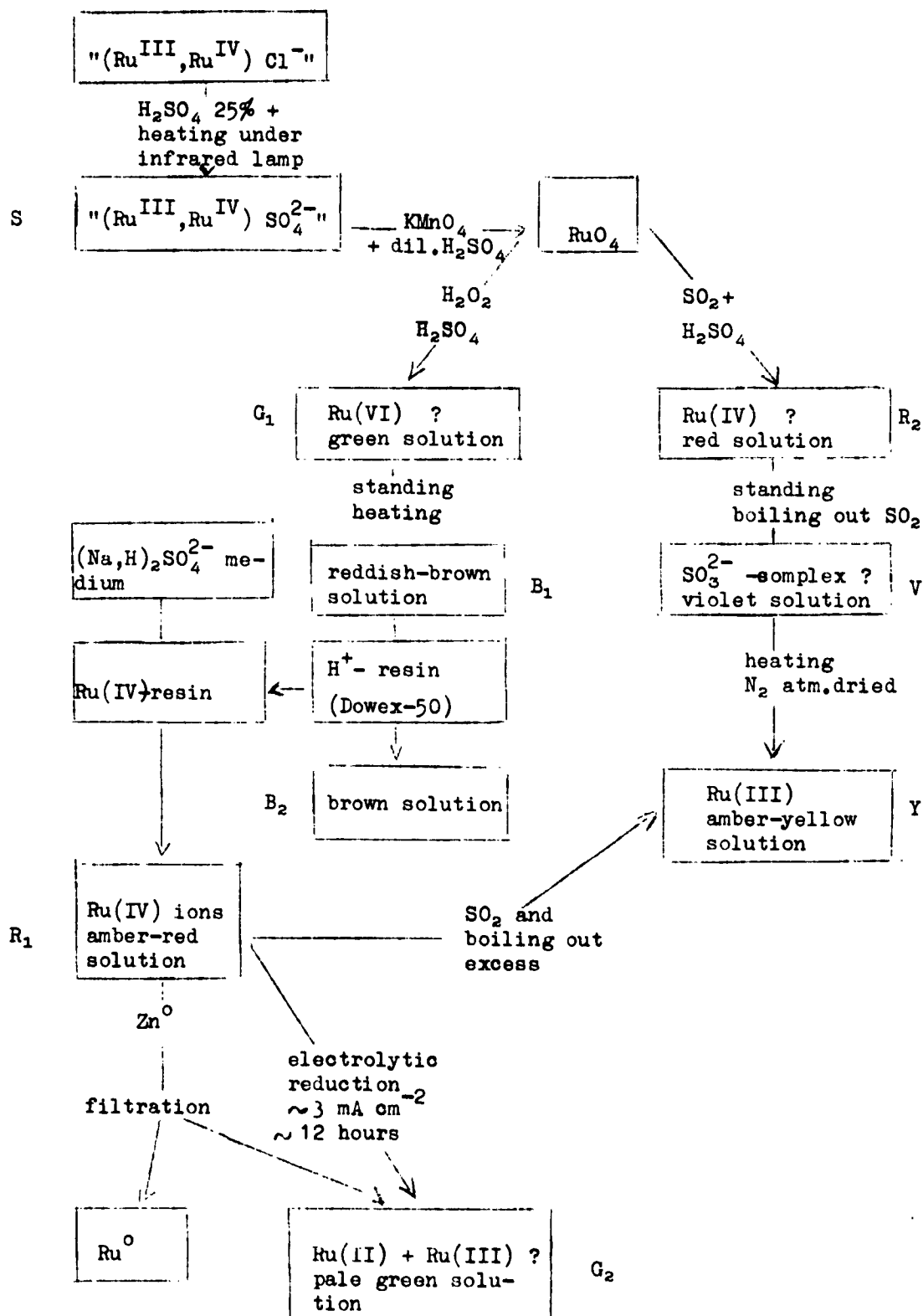
Green solution G<sub>1</sub>. To the initial ruthenium sulfate solution, S, an excess of KMnO<sub>4</sub> was added. The RuO<sub>4</sub> formed was distilled in an all-glass apparatus by heating and passing a slow stream of N<sub>2</sub>. The vapor was caught in three or four ice-cooled receivers containing 0.5 - 1 M H<sub>2</sub>SO<sub>4</sub> and an excess of H<sub>2</sub>O<sub>2</sub>. The solution, which was first yellow due to the RuO<sub>4</sub>, gradually turned green ("G<sub>1</sub>") with the evolution of O<sub>2</sub>. The absorption spectrum of G<sub>1</sub> has a maximum at 3000 Å. (Fig 1). With time, the solution gradually changed color and, after a couple of days, had turned reddish brown ("B<sub>1</sub>").

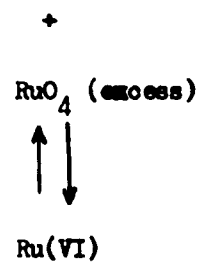
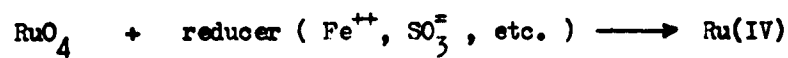
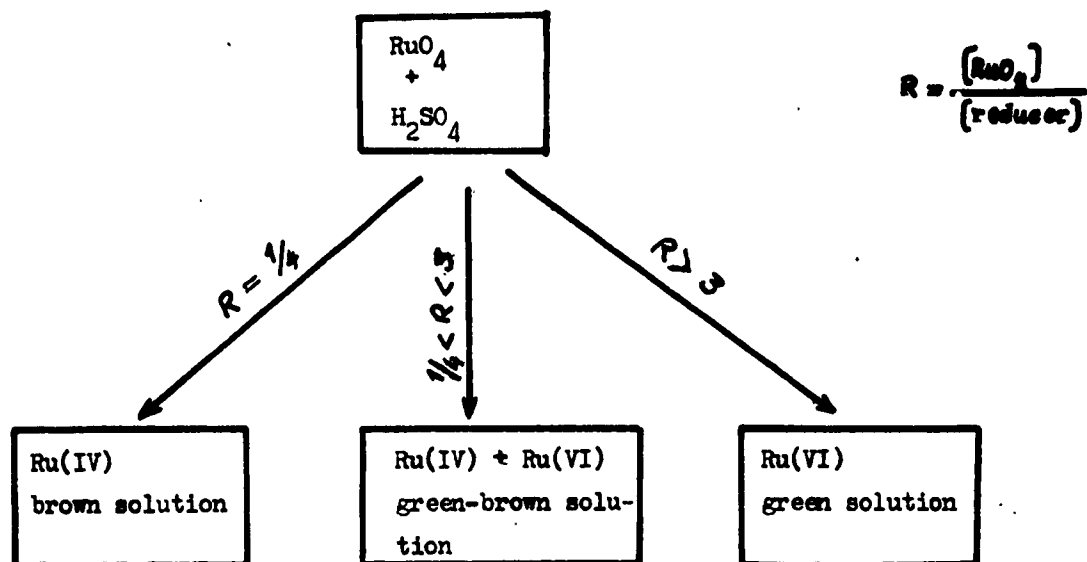
Solutions similar to G<sub>1</sub> have been prepared by other workers. Martin<sup>5</sup> (scheme II) reduced RuO<sub>4</sub> in H<sub>2</sub>SO<sub>4</sub> by means of NaNO<sub>2</sub>, Na<sub>2</sub>SO<sub>3</sub>, FeSO<sub>4</sub> etc, and obtained a green or greenish-brown solution, depending on the relative excess of Ru(VIII), which he suggested contained ruthenium(VI) or ruthenium(VI) + ruthenium(IV) sulfate complexes. El Guebely and Haissinsky<sup>6</sup> (scheme III) obtained a green solution by electrolytic oxidation of ruthenium(III) sulfate (E = 1.4 volt against a saturated calomel electrode) or by electrolytic reduction of RuO<sub>4</sub> in sulfate solutions (E = -0.2 volt). They claimed it contained ruthenium(VI). In neither case, however, were spectra given.

Wilson<sup>7</sup> reduced RuO<sub>4</sub> in dilute H<sub>2</sub>SO<sub>4</sub> with an excess of H<sub>2</sub>O<sub>2</sub> and obtained a solution for which he gives the spectra obtained after various times. The spectrum after about 9 days has a maximum at 2900 Å and coincides approximately with that of G<sub>1</sub> given here (Fig 1). He ascribed it to ruthenium(III). Using less H<sub>2</sub>O<sub>2</sub>, Wilson obtained, following Martin<sup>5</sup>, greenish-brown solutions. He suggested they might contain Ru in the valency states IV and VI. However, considering the reactions to be described in the following, it seems likely that the ruthenium species in G<sub>1</sub> has a higher valency state than +4, probably +6.



Schema I





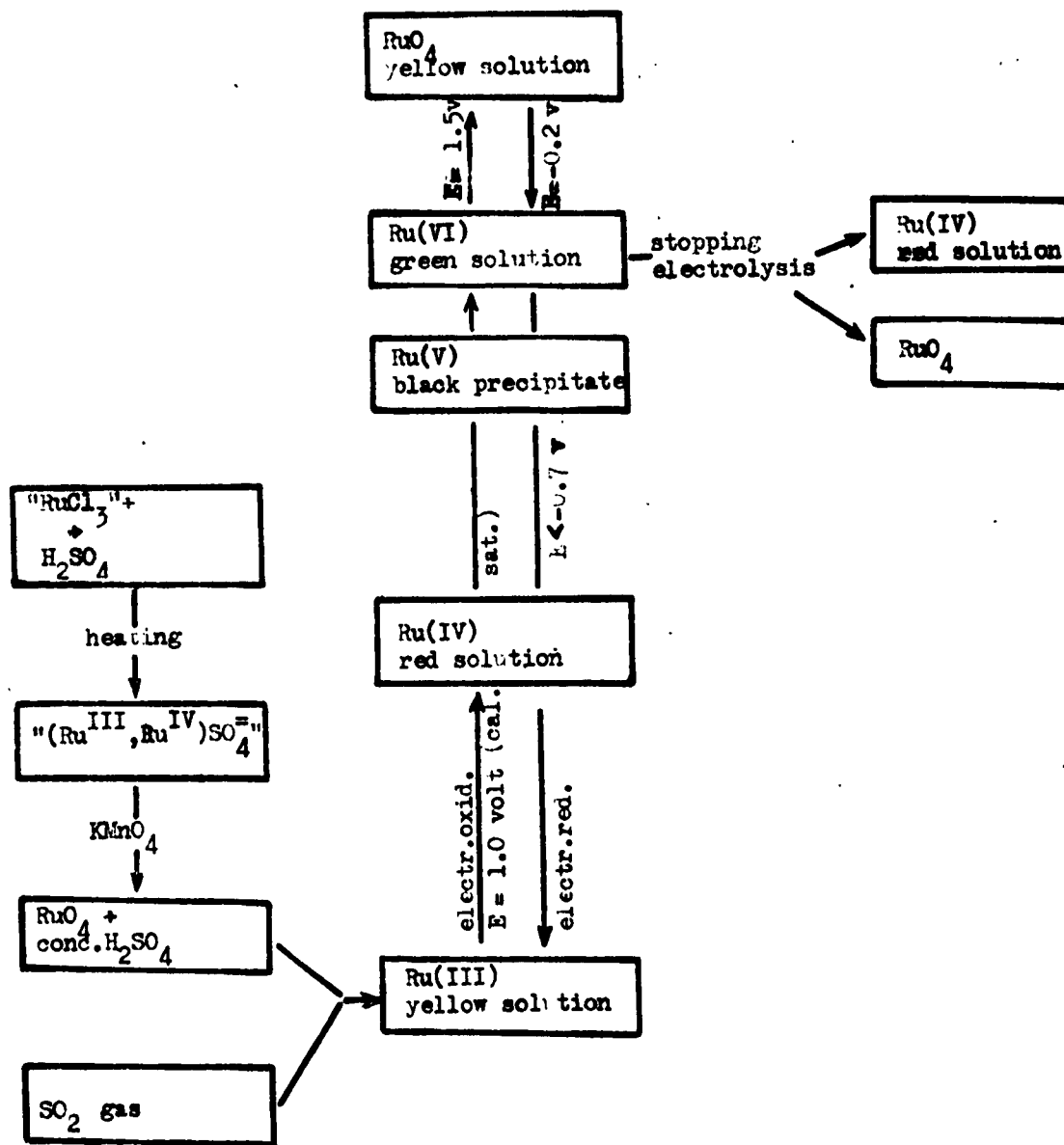


Fig. 2

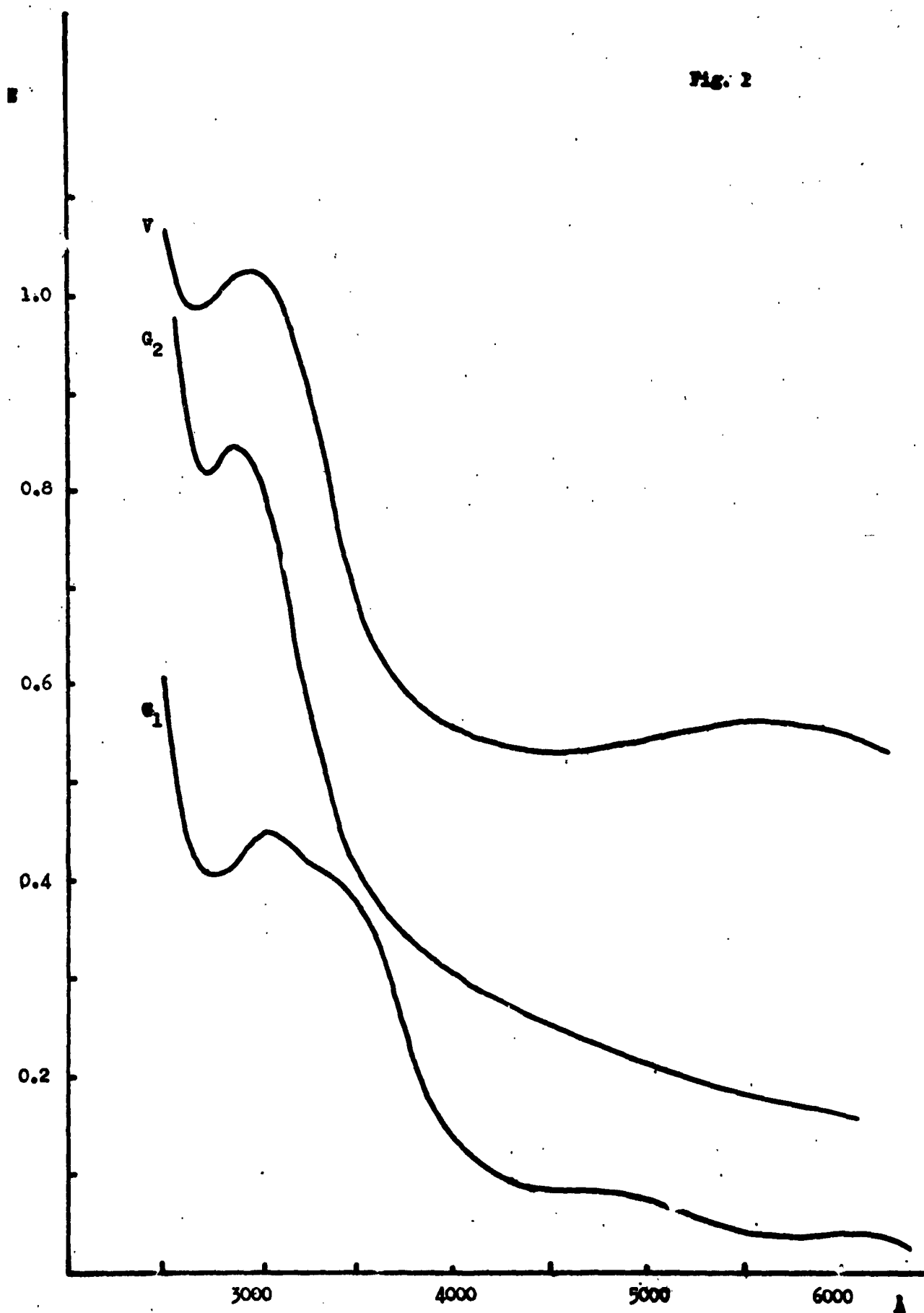
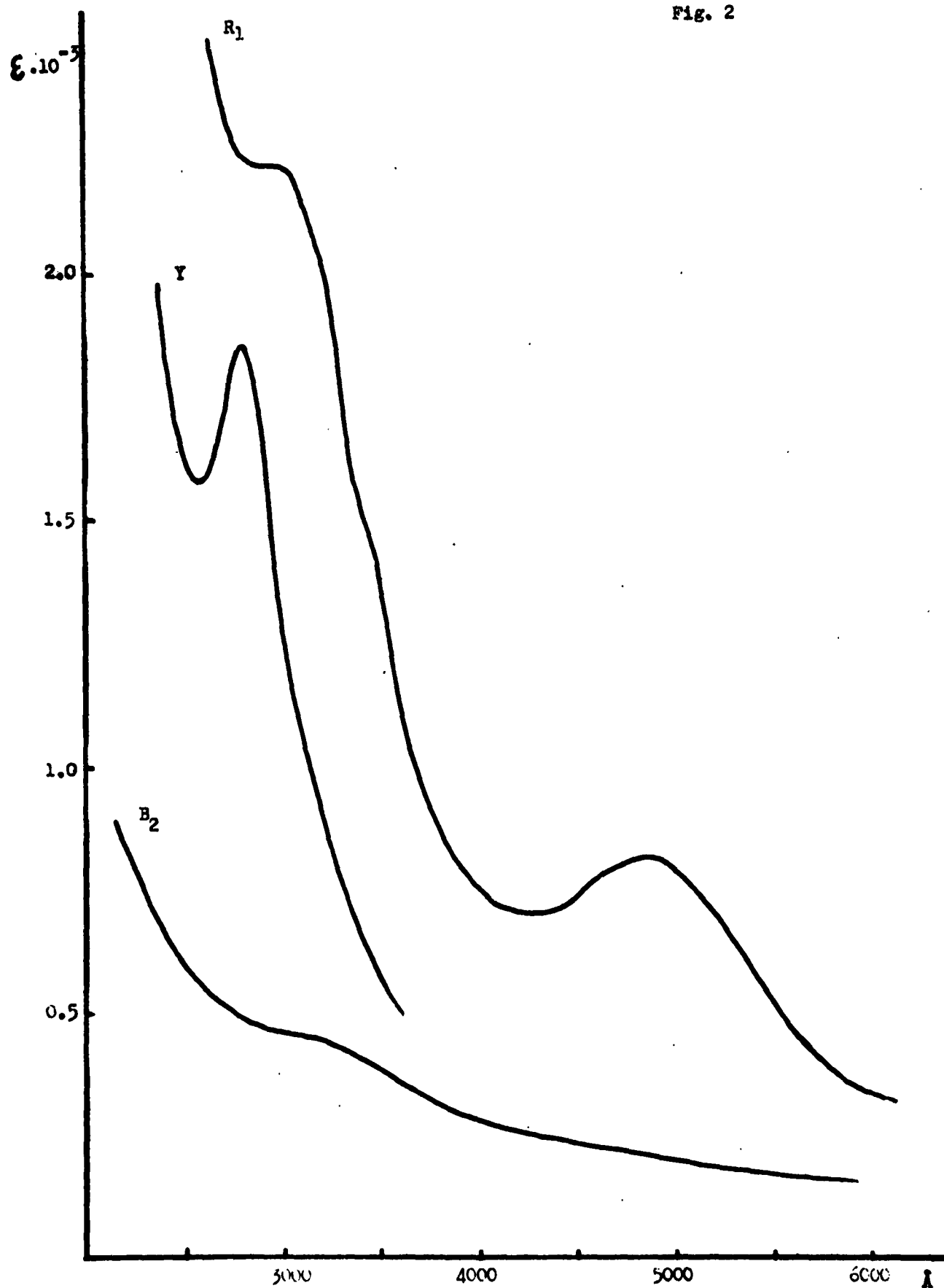


Fig. 2



The solutions  $B_1$ ,  $B_2$  and  $R_1$ . When the green solution  $G_1$  was kept for two or three days, it turned into a reddish-brown solution  $B_1$ , which was boiled to remove  $H_2O_2$ , cooled, diluted and then passed through a series of short columns with  $H^+$ -saturated Dowex-50 ion exchanger. A brown solution (" $B_2$ ") passed through the resin - it probably contained an uncharged or anionic sulfate complex. The resin which had turned reddish black, was washed repeatedly with distilled water and then with  $Na_2SO_4$  or  $(Na,H)_2SO_4$  solution a red solution (" $R_1$ ") being obtained. The spectra of  $B_2$  and  $R_1$  are given in Fig. 2.

For hydrolysis studies, a ruthenium(IV) sulfate solution of relatively low acidity can be conveniently prepared by eluting a cation exchanger, saturated with a red cationic species  $R_1$ , with a dilute  $Na_2SO_4$  solution and then concentrating by careful evaporation under vacuum at room temperature.

Solutions  $R_2$ , V and Y. In another series of experiments,  $RuO_4$  was collected in, say, 0.2 M  $H_2SO_4$  saturated with  $SO_2$ . In this case, rapid reduction was observed. The solution first turned reddish-brown with the same shade as  $R_2$  (no spectra could however be taken because of experimental difficulties) and then gradually turned yellowish brown. However, if the excess  $SO_2$  was not immediately boiled off, a violet solution ("V") was formed overnight, which was stable over a long time, even after the excess  $SO_2$  had been boiled off. When V was evaporated slowly to dryness with an electric mantle in a  $N_2$  atmosphere (free from  $O_2$ ) and the dry residue dissolved in dilute  $H_2SO_4$ , the solution was blackish brown when concentrated, and yellow ("Y"), when diluted. The spectra of V and Y are given in Figs. 1 and 2.

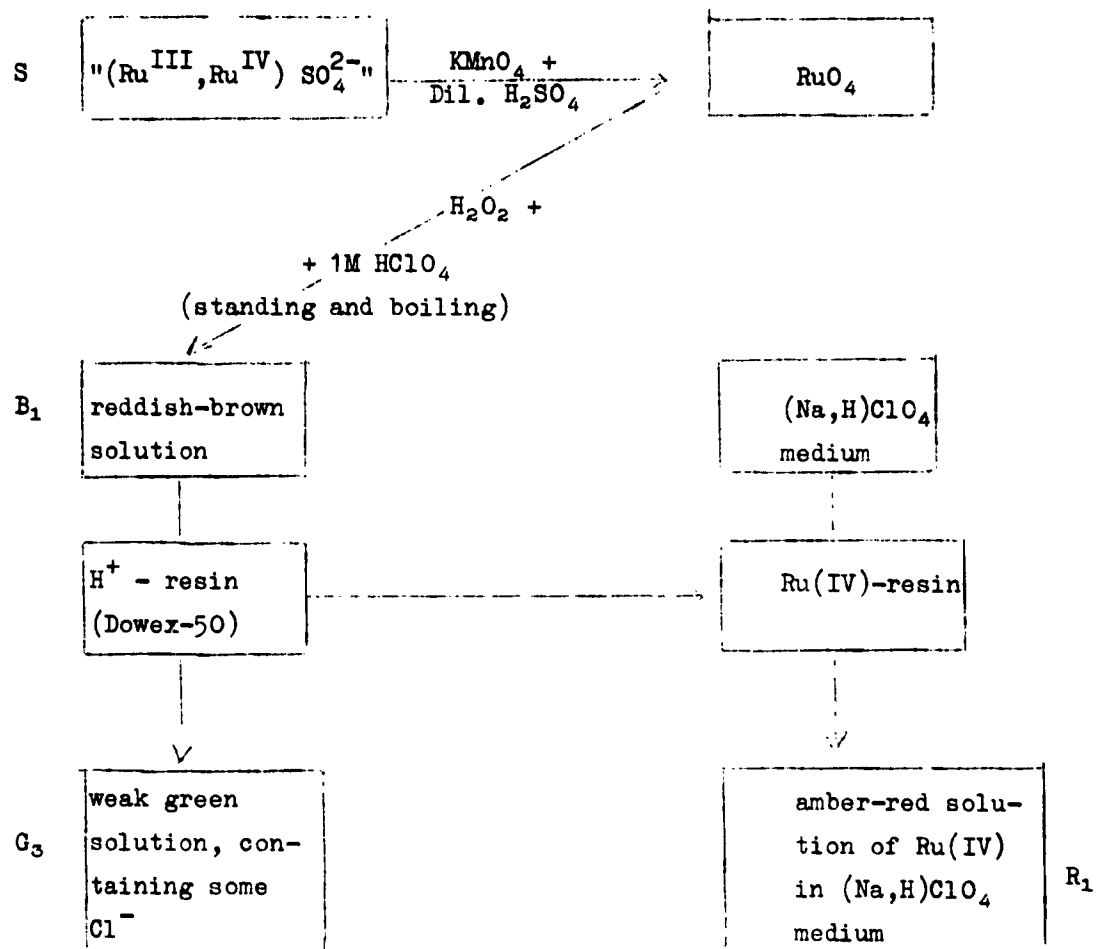
A similar yellow solution was obtained by El Guebeley and Haissinsky<sup>6</sup> (scheme III) who concluded that it contained ruthenium(III). We agree with their conclusion and consider that  $R_2$  contains ruthenium(IV) (see analysis below). The solution V is probably a strong sulfito complex of ruthenium(III).

#### Preparation of ruthenium(IV) in perchlorate medium

After some experience had been obtained with the behavior of ruthenium(IV), similar experiments were carried out in perchlorate medium. In this case, of course,  $SO_2$  could not be used as reducing agent, since this would have introduced sulfate ions in the solutions. The experiments are described in scheme IV.

$RuO_4$  was prepared as before and collected in 1 M  $HClO_4$  with an excess of  $H_2O_2$ . The solution was initially yellow from  $RuO_4$ , and on standing turned

Schema IV



reddish-brown ( $B_1$ ). No green intermediate could be observed, in contrast to the behavior in sulfate medium.

The solution  $B_1$  was boiled to remove the  $H_2O_2$ , diluted, and then, as with the sulfate, passed through a  $H^+$ -saturated ion exchanger. The resin turned reddish black, as in the sulfate case, but the solution which passed through contained a very low concentration of Ru and was pale green ( $G_3$ ). This solution  $G_3$  also contained some  $Cl^-$ , which was not present in  $B_1$ .

The resin was first washed repeatedly with distilled water and then with 3 M  $NaClO_4$  or 3 M  $(Na,H)ClO_4$ . The eluate was an amber-red solution  $R_1$  which contained ruthenium(IV) ions, but no detectable amount of  $Cl^-$ . On this latter solution,  $R_1$ , preliminary spectral and electrometric measurements have been made in order to study the hydrolysis (see below).

#### Analytical methods

The literature on the analysis of Ru, which has been reviewed by Beamish<sup>8</sup>, is rather meagre. Some gravimetric methods have been proposed, and also some colorimetric and volumetric (redox) methods; the latter especially seem somewhat uncertain. Hence it appeared desirable to check earlier methods and to search for new ones.

Weighing as metallic Ru. The most reliable method for determining the total Ru concentration seems to be by transformation to metallic Ru, and weighing as such. The transformation may be made in several ways:

a) A hydroxide is precipitated by adding 10 %  $NaHCO_3$  solution to pH ~6 (bromocresol purple). The hydroxide is filtered off from a boiling solution, washed, ignited, and reduced in  $H_2$ . This method<sup>11</sup> seems to work for many solutions of Ru(IV), but in certain cases, some Ru remains in the solution as an anionic complex.

b) A known amount of solution is added to a weighed crucible containing 1-2 ml strong  $NH_3$  soln. The crucible is kept under an infrared lamp till the contents have evaporated to dryness, after which it is heated in  $H_2$  to transform<sup>them</sup> to the metal. This method requires that there are no non-volatile constituents except Ru.

c) Because b) could not be used in solutions containing, say,  $Na^+$ , and since a) seemed somewhat uncertain, a third method was also tried out, namely direct reduction to Ru metal in the solution by adding a metal. Magnesium was found to be the most suitable one of those studied, and the reduction was carried out as follows:



To a known amount of solution, an excess of Mg metal and of dilute sulfuric acid are added. When the reaction has been almost completed at ordinary temperature, more  $\text{H}_2\text{SO}_4$  is added, and the solution is boiled in order to dissolve all excess of Mg and to agglomerate any colloidal Ru that may have been formed. The Ru is carefully collected on a weighed porcelain filter (Berlin 1 A 1), washed with 0.5 M  $\text{H}_2\text{SO}_4$  and water, heated in  $\text{H}_2$  and finally weighed as Ru.

Method c) was compared with a) and b) in the following way.

An  $\text{R}_1$  solution, containing  $\sim 0.6$  M H and  $\sim 2.4$  M  $\text{NaClO}_4$  was analyzed according to method a), with the addition that the precipitate was weighed also after heating but before the final reduction with  $\text{H}_2$ . The concentration of the original  $\text{R}_1$  solution was found, assuming the intermediate compound  $\text{RuO}_2$  to be  $9.61 \text{ mM}^x$ ,  $9.52 \text{ mM}^x$  (average  $9.57 \pm 0.05 \text{ mM}^x$ ). From the weight of the metallic Ru, the following concentrations were found, all in  $\text{mM}^x$ : 9.51, 9.65, 9.57, (average  $9.58 \pm 0.08 \text{ mM}^x$ ). The results indicate that the method is reproducible, and that the intermediate compound has a composition close to or equal to  $\text{RuO}_2$ .

The solution was now analyzed according to method c)

g of solution added	mg Ru weighed	B $\text{mM}^x$
6.1099	6.0	9.71
6.8632	6.7	9.51
17.8865	17.0	9.40
18.7361	18.0	9.50
Average $9.5 \pm 0.1$		

A solution Y, which is later shown to contain Ru as Ru(III) and 0.5 M in  $\text{H}_2\text{SO}_4$ , was analyzed by method b). The concentration was found to be, 32.15 mM, 31.65 mM, average  $31.90 \pm 0.25 \text{ mM}$ . Four 10.00 ml portions were analyzed, according to method c), and the amounts found were 31.9, 32.5, 32.5, and 31.9 mg, which gives 31.55 (twice) and 32.15 (twice) mM (average  $31.85 \pm 0.3 \text{ mM}$ ).

In an experiment with another solution Y also 0.5 M in  $\text{H}_2\text{SO}_4$ , the total Ru-concentration was found by method b) to be:

(21.71, 21.76, 21.75  $\text{mM}^x$ )                      average  $21.74 \pm 0.02 \text{ mM}^x$

and by method c) as:

(22.1, 21.6  $\text{mM}^x$ )                      average  $21.85 \pm 0.2 \text{ mM}^x$

■ Here, and in the following,  $\text{mM}^x$  means millimoles per 1000 g solution.

These experiments show that method c) is reproducible. Even if the spread is somewhat greater than with method a) and b) the average is the same, within the experimental error, so that it can be used with confidence. The advantage of method c) is that it is applicable both to Ru(III) and Ru(IV), and to cationic species as well as to anionic ones, whereas method a) is not feasible if the solution contains strong anionic complexes. For instance, from B<sub>2</sub>, the precipitation of the hydroxide is not complete.

Redox titration. Oxidation state of Ru in R<sub>1</sub>. In order to find the oxidation number of Ru in the R<sub>1</sub>-solution, which seemed to be a rather well-defined and stable form of Ru, the following procedure was used:

To a known amount of an R<sub>1</sub> solution, a known amount of standard cerium(IV) sulfate solution was added, and sulfuric acid, so that in the final solution [H<sup>+</sup>] was 3 to 4 M. The RuO<sub>4</sub> formed was removed by boiling the solution and passing N<sub>2</sub> through it. After that, the solution was cooled and back-titrated with Fe(II) + ferroin.

The results are given in the following table:

Ru $\mu$ moles	$\mu$ mol Ce <sup>4+</sup> required	Ce <sup>4+</sup> /Ru
46.5	186.2	4.00
	187.1	4.02
	187.9	4.04
	187.4	4.03
	185.7	3.99
	186.5	4.01
	187.7	4.04
	186.2	4.00

As seen from the last column four ( $4.02 \pm 0.02$ ) mmoles of Ce<sup>4+</sup> were consumed for each mmole of Ru to transform it to RuO<sub>4</sub>. This indicates that in the R<sub>1</sub> solution, ruthenium is present in the oxidation state IV.<sup>xx</sup>

When we assumed that the solutions contained Ru(IV) and used the titrations to determine its concentrations, we obtained  $9.35 \pm 0.05$  mM ( $9.30 \pm 0.1$  by weighing as Ru).

<sup>xx</sup>Note: Recently, Cortsema and Cobble<sup>9</sup> have published a preliminary note on the action of Ce(IV) and Cr(VI) on acidic solutions of Ru(IV), prepared by reduction of RuO<sub>4</sub> with H<sub>2</sub>O<sub>2</sub> or Fe(II) in aqueous solution.

According to these authors the solutions obtained, which should correspond to our B<sub>1</sub> solution, contained mainly hydrolyzed Ru(IV) polymers, corresponding to the addition of RuO<sub>2</sub>(H<sub>2</sub>O)<sub>x</sub> units to monomeric RuO<sup>2+</sup>.

The Ce(IV) titration method can thus be used for determining the total Ru concentration, B. Especially for dilute Ru(IV) solutions it allows a better precision than does the weighing of Ru. For example a solution in 0.2 M  $\text{H}_2\text{SO}_4$  was studied. Weighing of Ru gave  $2.2 \pm 0.1$  mM

With Ce(IV) titration we obtained  $2.18 \pm 0.03$  mM, as can be seen from the following table:

ml solution	$\mu\text{mole Ce}^{4+}$ required	Ru mM
6.00	52.3	2.18
"	52.5	2.19
"	51.6	2.15
"	52.4	2.18

Another solution of  $\text{pH} \sim 3.5$  had been obtained by eluting a cation exchanger with 0.25 M  $\text{Na}_2\text{SO}_4$ .

Weighing of Ru gave	$0.6 \pm 0.1$ mM
With Ce(IV) titration we obtained	$0.57 \pm 0.01$

ml solution	$\mu\text{mole Ce}^{4+}$ required	Ru mM
13.60	31.5	0.58
	30.4	0.56
6.00	13.6	0.57
	13.4	0.56

Oxidation number of Ru in solution Y. To determine the oxidation number of Ru in the solution denoted as Y, the following procedure was used: From a solution of Ru(IV) ( $=R_1$ ) of known concentration ( $B = 2.18 \pm 0.03$  mM) a known volume was taken out (in some cases the sample was weighed).  $\text{SO}_2$  was bubbled through, after which excess  $\text{SO}_2$  was removed by bubbling through  $\text{CO}_2$  and then by prolonged boiling. To this sample, which should correspond to Y in scheme I, excess of Ce(IV) was added,  $\text{RuO}_4$  was removed, and  $\text{Ce}^{4+}$  back-titrated with  $\text{Fe}^{2+}$  as before. The results are given in the following

Note, continued:

They found that the monomeric  $\text{RuO}^{2+}$  requires four oxidation equivalents, but with increasing polymerization they found a continuous increase in the number of equivalents required, and also a regular change in spectra and in extinction coefficients. They concluded that excess of oxidizing agent is needed for a simultaneous oxidation of bound water in the polymer.

In our experiments with the "purified"  $R_1$  solutions, it seems that always 4.00 Ce(IV) are needed per Ru; the spectra and extinction coefficients of  $R_1$  seem to remain almost constant (Fig 3). It might be of interest, however, to study further the action of oxidizing agents on  $B_1$  and on the fraction removed,  $B_2$ ; hitherto we have considered this to contain mainly neutral and anionic Ru complexes.

table: On the average five ( $5.05 \pm 0.05$ ) mmoles  $\text{Ce}^{4+}$  were needed to transform one mmole Ru to  $\text{RuO}_4$ , which indicates that ruthenium was present as Ru(III) in Y.

Ru $\mu\text{moles}$	$\mu\text{moles Ce}^{4+}$ required	$\text{Ce}^{4+}/\text{Ru}$	B mM
17.44	87.3	5.01	2.19
	87.0	5.00	2.18
	87.0	5.00	2.18
17.88	96.1	5.37	2.34
	95.8	5.36	2.34
	95.0	5.31	2.33
16.57	81.3	4.91	2.14
	80.7	4.87	2.12
	80.7	4.87	2.12
12.04	61.7	5.12	2.23
	62.9	5.22	2.28
	63.0	5.22	2.28
	61.4	5.10	2.21
9.56	46.0	4.81	2.09
	47.0	4.92	2.14
	47.1	4.93	2.14
	46.6	4.87	2.11

Average  $2.20 \pm 0.2$

The last column gives the concentration, B, calculated from the redox data, assuming Ru to be present as Ru(III).

#### Determination of $\text{H}^+$ excess and total anions in Ru(IV) solution

For the hydrolysis studies, it was necessary to determine, in addition to the total concentration of ruthenium (B), also the analytical excess of  $\text{H}^+$  (H). We shall define H as the analytical concentration of  $\text{H}^+$ , assuming all Ru to be in the form of  $\text{Ru}^{4+}$ . (Other definitions, for instance starting with  $\text{Ru}(\text{OH})_3^+$  are also conceivable, but this is the one we shall use.) In solutions of low acidity H may be negative.

The following methods were tried:

a) The solution of Ru(IV),  $R_1$ , is passed through a  $\text{H}^+$ -saturated ion exchanger and the eluate titrated as  $\text{H}^+\text{ClO}_4^-$ , (or  $\text{H}_4^+\text{SO}_4^{2-}$ ) with standard NaOH. In this way, the total anion concentration is obtained. If the solution contains no  $\text{Na}^+$  ions, the result will be  $(\text{H} + 4 \text{ B})$ .

b) To the Ru(IV) solution, standardized NaOH, containing enough acetylacetone to react with the Ru, is added from a buret, and the pH changes

followed with a glass electrode. The end point is determined graphically by Gran's method<sup>12</sup>. If, as we shall assume, Ru forms with acetylacetone (AH) an uncharged complex, say  $\text{RuA}_4$  or  $\text{RuOA}_2$  and  $\text{Na}^+$  does not react, then this method should give  $(H + 4B)$ , independent of whether  $\text{Na}^+$  is present or not. If there is no  $\text{Na}^+$ , b) is equivalent with a).

c) Standard NaOH is added to the Ru(IV) solution from a buret, and pH changes are followed with a glass electrode. The end point is indicated by a jump of nearly 200 mV in the measured emf. If we assume that at the equivalence point (around pH = 6-7) all Ru is present as a precipitate of  $\text{RuO}_2(\text{H}_2\text{O})_x$  the method should again give  $(H + 4B)$ ; c) is then equivalent to b).

In one series of experiments, 5 ml of a certain Ru(IV) solution, containing no  $\text{Na}^+$  ( $B \sim 1 \text{ mM}$ ) required

- a) 2.78 ml 247.2 mM NaOH;  $H + 4B = 137.4 \text{ mM}$
- b) 5.57 ml 123.6 mM NaOH (50 mM HA);  $H + 4B = 137.7 \text{ mM}$
- c) 5.55 ml 123.7 mM NaOH;  $H + 4B = 137.3 \text{ mM}$ .

In other, similar sets, the agreement was similar. The concordance between the three methods indicated that there is no serious error from the retention of perchlorate in the ion exchanger, and that  $\text{RuO}_2(\text{H}_2\text{O})_x$  seems to precipitate completely, without retaining any perchlorate, at least at low Ru concentrations.

Since method c) seemed to be the simplest one to use and also allowed simultaneous analysis for Ru, it was used in the following, finding the equivalence point with bromocresol purpur (pH =  $\sim 6$ ) as indicator. Before the end point, the solution was boiled in order to agglomerate the precipitate and make the indicator color more clearly visible. It was then cooled, and the titration finished.

An example of the reproducibility attained is given in the following figures. For a solution 3 M in  $(\text{Na})\text{ClO}_4$  and  $9.56 \text{ mM}^x$  in Ru:

7.0737 g solution required	33.69 ml 100.6 mM NaOH ;	$H + 4B = 479.1 \text{ mM}^x$
3.8786	18.43	478.0
2.1679	10.35	480.3

The experiments so described do not exclude however the possibility of a small systematic error in the composition of the precipitate in method c). This point will be elucidated by experiments on solution of high B and low H.

### Hydrolysis of Ru(IV) in 3 M (Na)ClO<sub>4</sub> medium. Preliminary results.

There is very little information in the literature concerning the species of Ru(IV) present in aqueous solutions. Anderson and McConnell<sup>10</sup>, from pH titrations in varying ionic medium, concluded that  $\text{Ru}(\text{OH})_2^{2+}$ ,  $\text{Ru}(\text{OH})_3^+$ , and a polynuclear hydroxo-complex were present but that there was no evidence for the unhydrolyzed  $\text{Ru}^{4+}$  ion. Starik and Kositsyn<sup>13</sup> from solubility measurements concluded that the main species was  $\text{Ru}(\text{OH})_3^+$ .

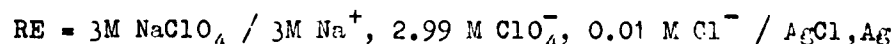
We have tried to measure the extinction curve for Ru(IV) solutions  $R_1$  3 M in (Na)ClO<sub>4</sub> medium at various acidities, between 0.0046 and 3 M, and with B between 4 and 12 mM. It is a remarkable fact that the molar extinction curve (Fig. 3) seems to be constant, within the experimental errors. The curve has three maxima, which, incidentally, might be used for analytical purposes: 3000 Å with  $\epsilon = 2173 \pm 10 \text{ M}^{-1}\text{cm}^{-1}$  at 4800 Å with  $\epsilon = 693 \pm 5 \text{ M}^{-1}\text{cm}^{-1}$ , and 8800 Å with  $\epsilon = 105 \pm 1 \text{ M}^{-1}\text{cm}^{-1}$ . The measurements were made with a Hilger Uvispec spectrophotometer, with cells of 0.101 and 1.00 cm thickness.

The spectroscopic data (also given in Table I) seem to indicate that, at least in the range between 0.004 and 3 M  $\text{H}^+$  only one species predominates in the Ru(IV) solutions. It is of interest to determine its composition.

We shall introduce the quantity Z, which gives the number of  $\text{OH}^-$  groups bound per Ru. The relationship between Z, H, B, and the free concentration  $[\text{H}^+] = h$  is:

$$h - H = BZ \quad (1)$$

In order to determine Z, the following experiment was carried out. To a known amount ( $v_0$  ml) of Ru(IV) solution 3 M in (Na,H) ClO<sub>4</sub> medium,  $v$  ml of HClO<sub>4</sub> or NaHCO<sub>3</sub> in the same medium were added from a buret, the e.m.f. of a glass electrode in combination with the half-cell



was determined. For more acidic solutions weighed amounts of purest NaHCO<sub>3</sub> were added instead, and the e.m.f. measured after each addition of solid.

For the e.m.f. of the cell

+ glass electrode / Ru(IV) solution / RE + -

the following formula should be valid :

$$E = E_0 - E_j + 59.15 \log h \quad (2)$$

The values were plotted, using the Gran function<sup>12</sup>:

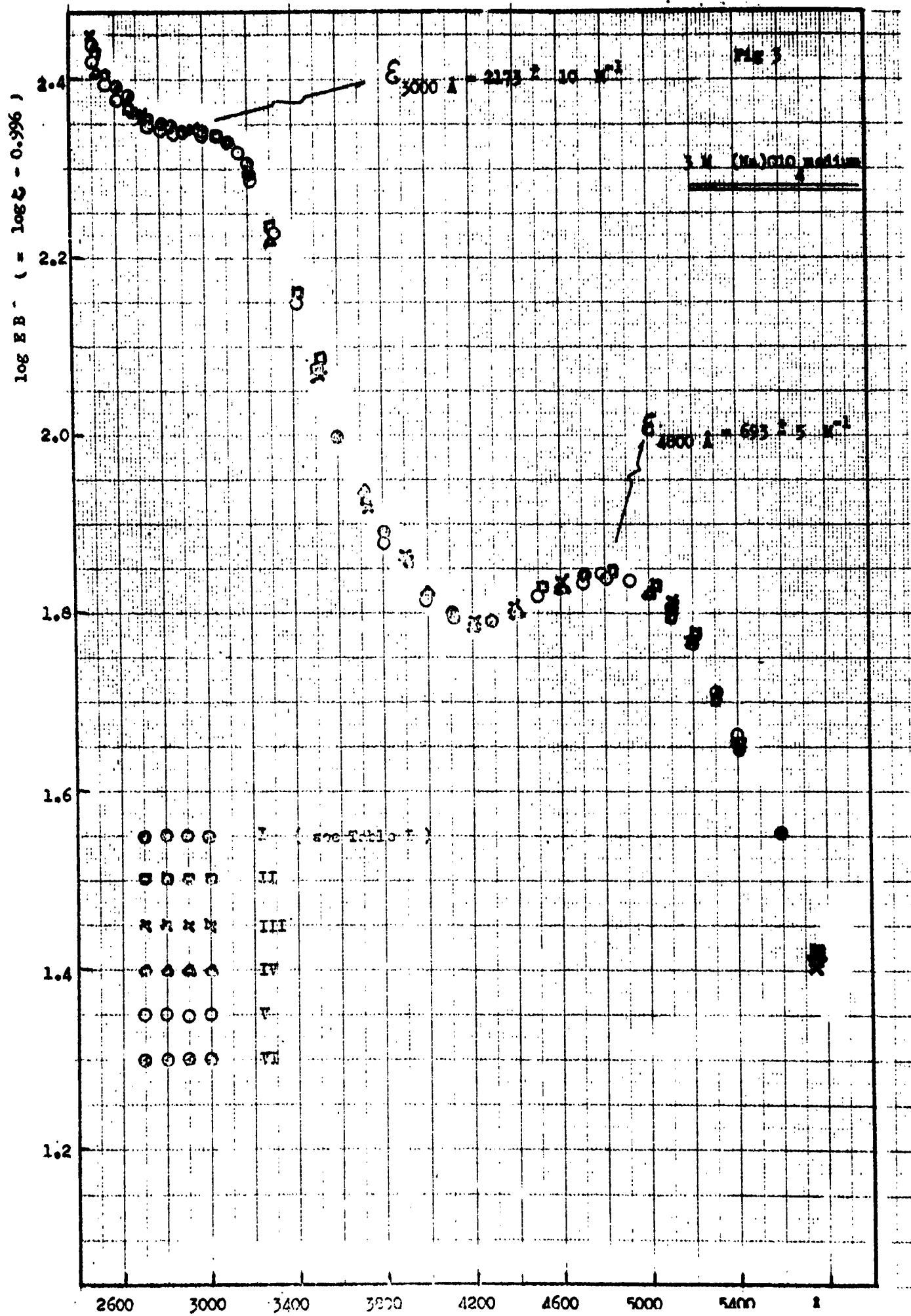


Fig. 3 (continuation)

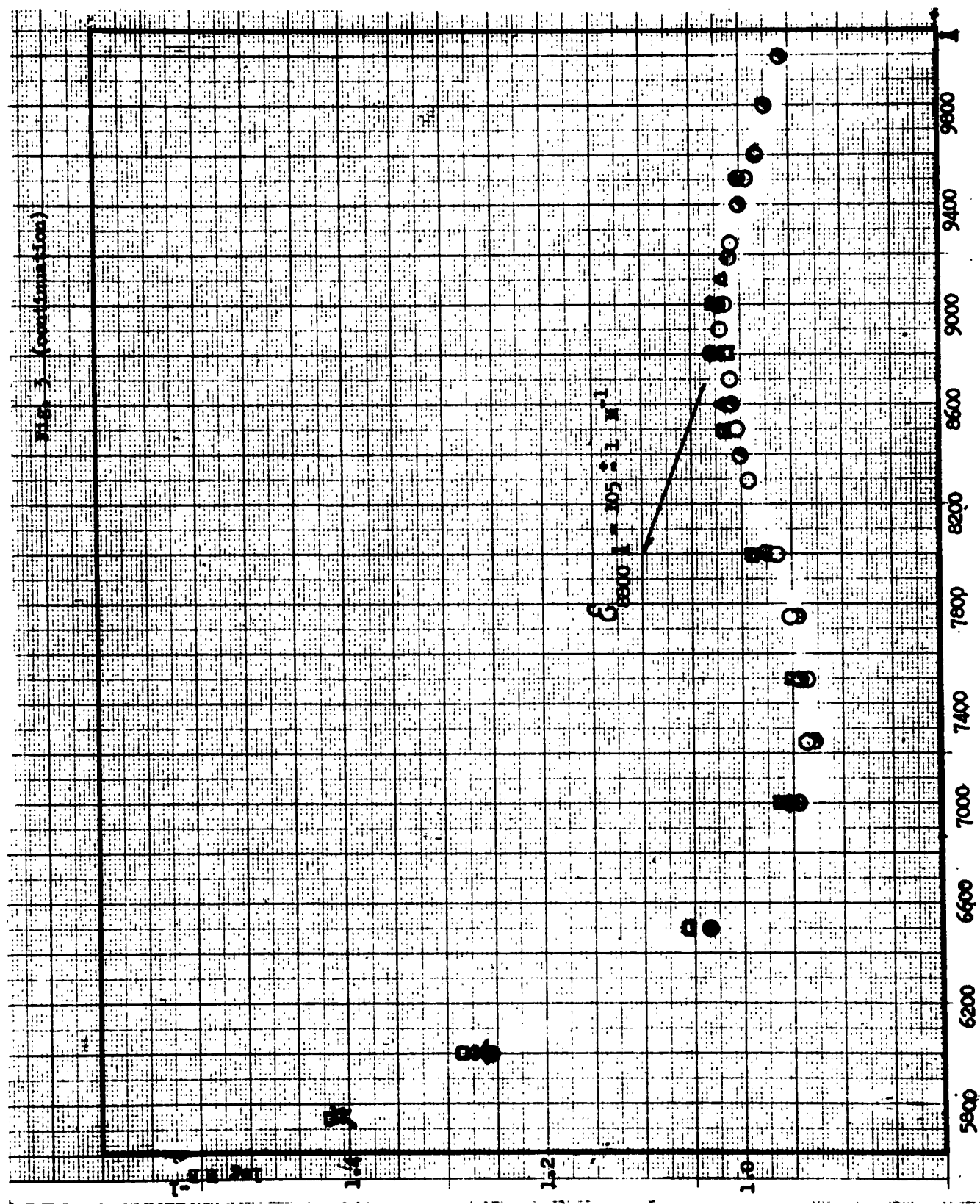




Table I. - Values of  $\log E B^{-1}$  ( $= \log \epsilon - 0.996$ ) for different wavelength  
B and H.

	I	II	III	IV	V	VI
	B = 12 mM	B = 4.8 mM	B = 4.8 mM	B = 4.8 mM	B = 4.2 mM	B = 3.6 mM
$\lambda \text{ \AA}$	H $\approx$ 200 mM	H $\approx$ 3 mM	H $\approx$ 100 mM	H $\approx$ 680 mM	H $\approx$ 9 mM	H $\approx$ 600 mM
2500	-	2.427	2.418	2.421	2.417	2.435
2550	-	2.400	-	-	2.389	2.408
2600	-	2.382	2.377	2.379	2.373	2.391
2650	-	2.371	-	-	2.362	2.377
2700	-	2.362	2.358	2.358	2.352	2.367
2750	-	2.354	-	-	2.346	2.358
2800	2.348	2.346	2.342	2.342	2.340	2.350
2850	2.339	2.342	-	-	2.335	2.344
2900	2.340	2.342	2.339	2.340	2.337	2.344
2950	2.342	2.342	2.339	2.342	2.339	2.346
3000	2.340	2.342	2.340	2.342	2.340	2.346
3050	2.339	2.340	2.339	2.341	2.338	2.344
3100	2.332	2.332	2.332	2.333	2.330	2.337
3150	2.316	2.316	2.318	2.319	2.315	2.320
3200	2.297	2.292	2.295	2.297	2.293	2.299
3250	2.238	2.233	2.233	2.236	2.232	2.238
3400	-	2.161	2.168	2.160	2.156	2.161
3500	-	2.079	-	2.078	-	2.079
3700	1.935	1.936	1.930	1.934	-	1.935
3800	1.892	1.889	1.881	1.898	1.879	1.885
3900	1.848	1.852	-	1.848	1.843	1.850
4000	1.820	1.823	1.812	1.818	1.814	1.820
4100	1.798	1.803	-	-	1.794	1.799
4200	1.792	1.799	1.788	1.792	1.786	1.791
4300	1.798	1.805	-	1.800	1.791	1.797
4400	1.812	1.818	1.808	1.813	1.804	1.808
4500	1.827	1.832	1.823	1.828	1.818	1.825
4600	1.836	1.844	1.833	1.838	1.831	1.838
4700	1.843	1.850	1.839	1.844	1.836	-
4800	1.845	1.851	1.843	1.844	1.840	1.846
4900	1.843	1.845	1.839	1.841	1.836	1.843
5000	1.832	1.833	1.825	1.829	1.827	1.829
5100	1.808	1.807	1.803	1.803	1.804	-
5200	1.769	1.772	-	-	1.768	-
5300	1.720	1.720	1.712	1.714	1.715	-
5400	1.650	1.655	-	-	1.650	-
5600	1.578	-	-	-	-	-
6000	-	1.288	1.263	1.274	-	1.256
6500	-	1.059	-	-	-	1.034
7000	-	0.962	-	-	0.950	0.950
7500	-	0.952	-	-	0.938	0.949
8000	0.973	0.991	-	0.981	0.968	0.987
8500	1.013	1.018	-	-	1.010	-
8700	-	-	-	-	1.010	-
8800	1.029	1.025	-	1.026	-	1.017
8900	-	-	-	-	1.020	-
9000	1.021	1.025	-	-	1.020	1.017
9500	1.000	-	-	-	1.000	-

$$F = (v + v_0) 10^{(E - E'_0 - E_j)/59.15} = (v + v_0) h \cdot 10^{(E_0 - E'_0)/59.15} = h (v + v_0) k^{-1}; (k = \text{constant}) \quad (3)$$

(In those cases where the titrations were made by weight, the weights should be inserted instead of  $v_0$  and  $v$ , and the concentrations expressed in moles per kg solution ( $M^{\text{kg}}$ ).  $E'_0$  is a round value taken at random such as 300 mV. For  $E_j$ , the expression  $E_j = 0.02 h$  was used).

Denoting the initial values for H and B by  $H_0$  and  $B_0$ , and the concentration of  $\text{NaHCO}_3$  in the buret by  $c$  (or  $\text{HClO}_4$  by  $(-c)$ ), we have,

$$(v + v_0) H = v_0 H_0 - v c \quad (4)$$

$$(v + v_0) B = v_0 B_0 \quad (5)$$

Now, from equations (1), (3), (4) and (5) it follows that:

$$kF = (v + v_0) h = v_0 H_0 + v_0 B_0 Z - v c \quad (6)$$

When  $F$ , which can be calculated from experimental data with equation (3), is plotted against  $v$ , it is found that  $F(v)$  is practically a straight line. This indicates that  $Z$  is constant, since  $v_0$ ,  $H_0$  and  $B_0$  are constants.

The plot  $F(v)$  was extrapolated to  $F=0$ ; the line intersects the horizontal axis at  $v_t$ . From (5) and (6) we obtain,

$$v_t c = v_0 (H_0 + B_0 Z) \quad (7)$$

The following table gives the results obtained with four different solutions. The first was obtained by eluting ion exchange resin with a 3M (Na, H) $\text{ClO}_4$ ,  $H \sim 0.44 \text{ mM}^{\text{kg}}$ . The second solution was made by adding a known amount of  $\text{NaHCO}_3$  to the first one. The third solution was made by eluting a resin with 3 M  $\text{NaClO}_4$ , and the fourth by adding 3 M (H, Ru(IV), Na) $\text{ClO}_4$  to the third.

$B_0$	$H_0 + 4B_0$	$H_0 + B_0 Z$	$Z$	
9.56 $\text{mM}^{\text{kg}}$	479 $\text{mM}^{\text{kg}}$	469.6 $\text{mM}^{\text{kg}}$	3.0	Fig. 4
9.38 $\text{mM}^{\text{kg}}$	12.7 $\text{mM}^{\text{kg}}$	3.3 $\text{mM}^{\text{kg}}$	3.0	Fig. 5
4.2 mM	8.8 mM	4.6 mM	3.0	Fig. 6
2.1 mM	24.1 mM	22.0 mM	3.0	Fig. 7

As can be seen the data indicate that  $Z = 3$ , and thus the complex should be  $\text{Ru}(\text{OH})_3^+$ , or a polymer of it. At least for  $h > 10^{-3}$ , there seems to be little hydrolysis of this species; at  $h < 10^{-4}$  values, unstable e.m.f. values were observed, presumably due to colloidal precipitation.

From the value for  $Z$  it is possible to calculate independent values of  $h$ , from  $H$ ,  $B_0$  and  $Z$  at each point, and then to plot  $E - 59.15 \log h$

( $-E_o - E_j$ ) as a function of  $h$ . Fig. 8 gives such a plot for a solution free from ruthenium; it is linear as expected (open circles). The black points in Fig. 8 were obtained with a solution with  $B \sim 2$  mM; this plot is also linear, except at <sup>the</sup>very lowest values for  $h$ . This diagram also agrees with the assumption that  $Z$  is constant in acid solutions. However, no certain conclusions can be drawn concerning further hydrolysis in solution at the very lowest  $h$ .

It is intended to get additional data on these reactions.

Fig. 4

3M (Na)ClO medium

vessel = 44.8729 g.,  $B_0 = 9.56 \text{ mm}^2$  and

$(H_0 + 4B_0) = 479 \text{ mm}^2$ ,  $R_0(IV)$

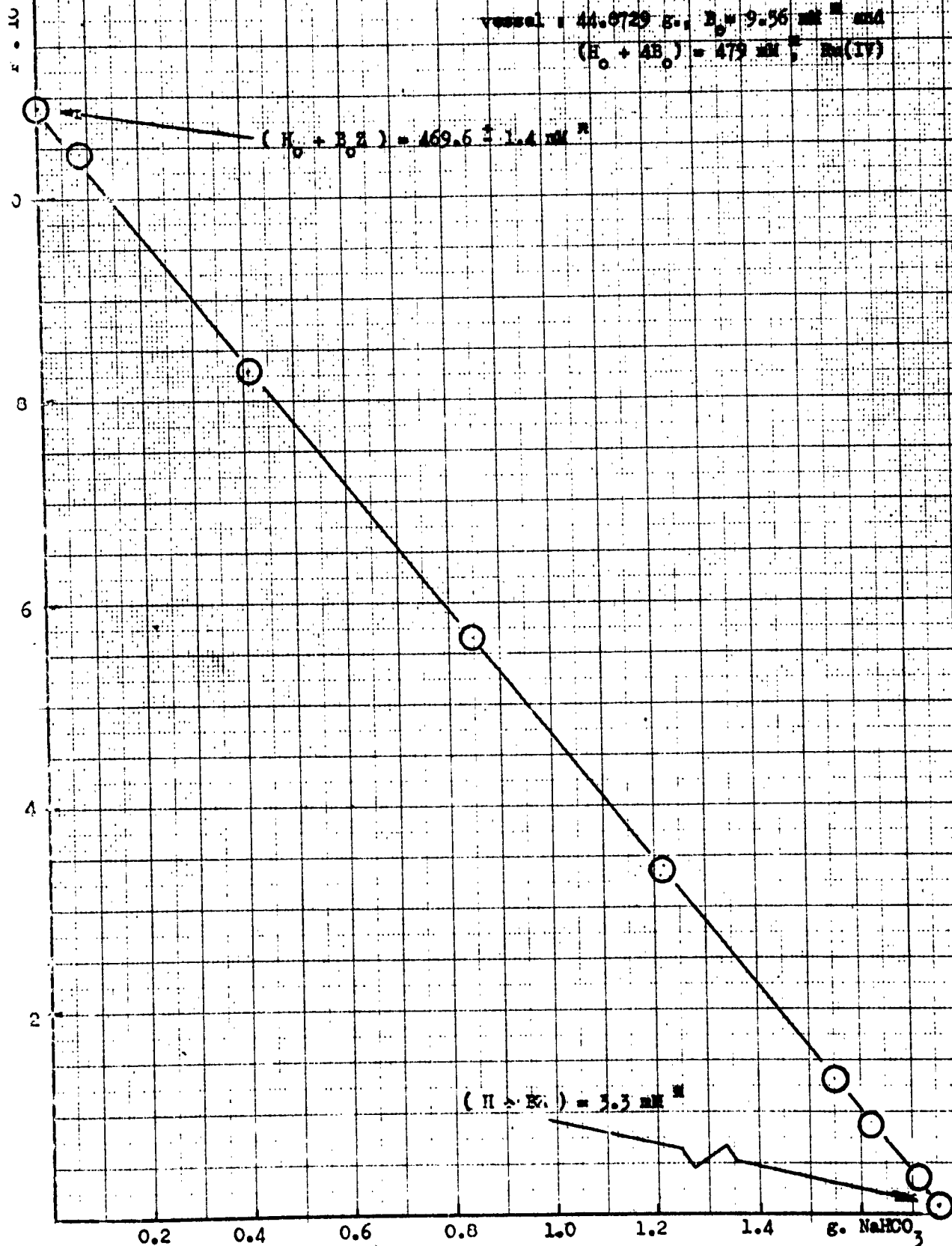


Fig. 5

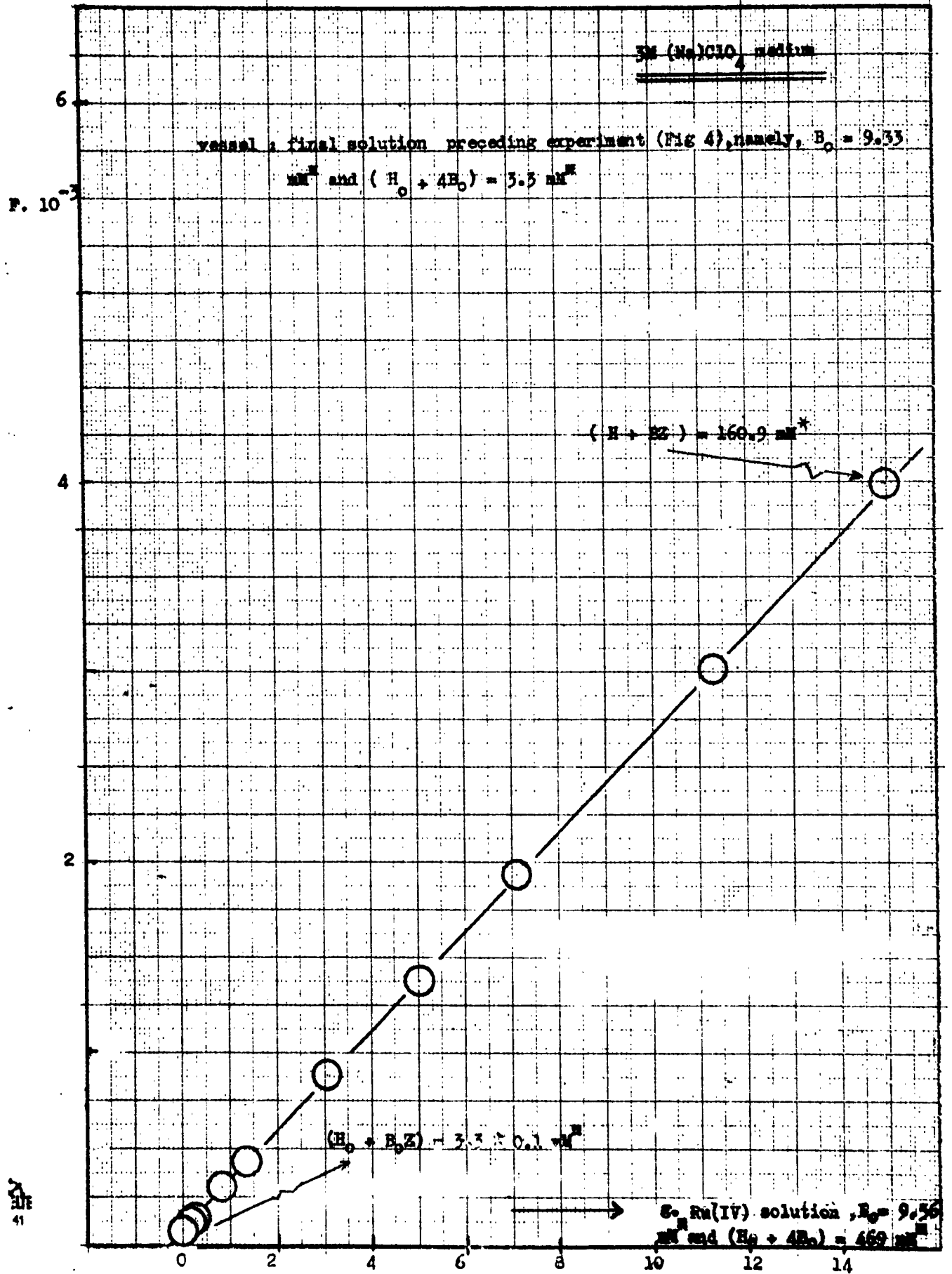


Fig. 6

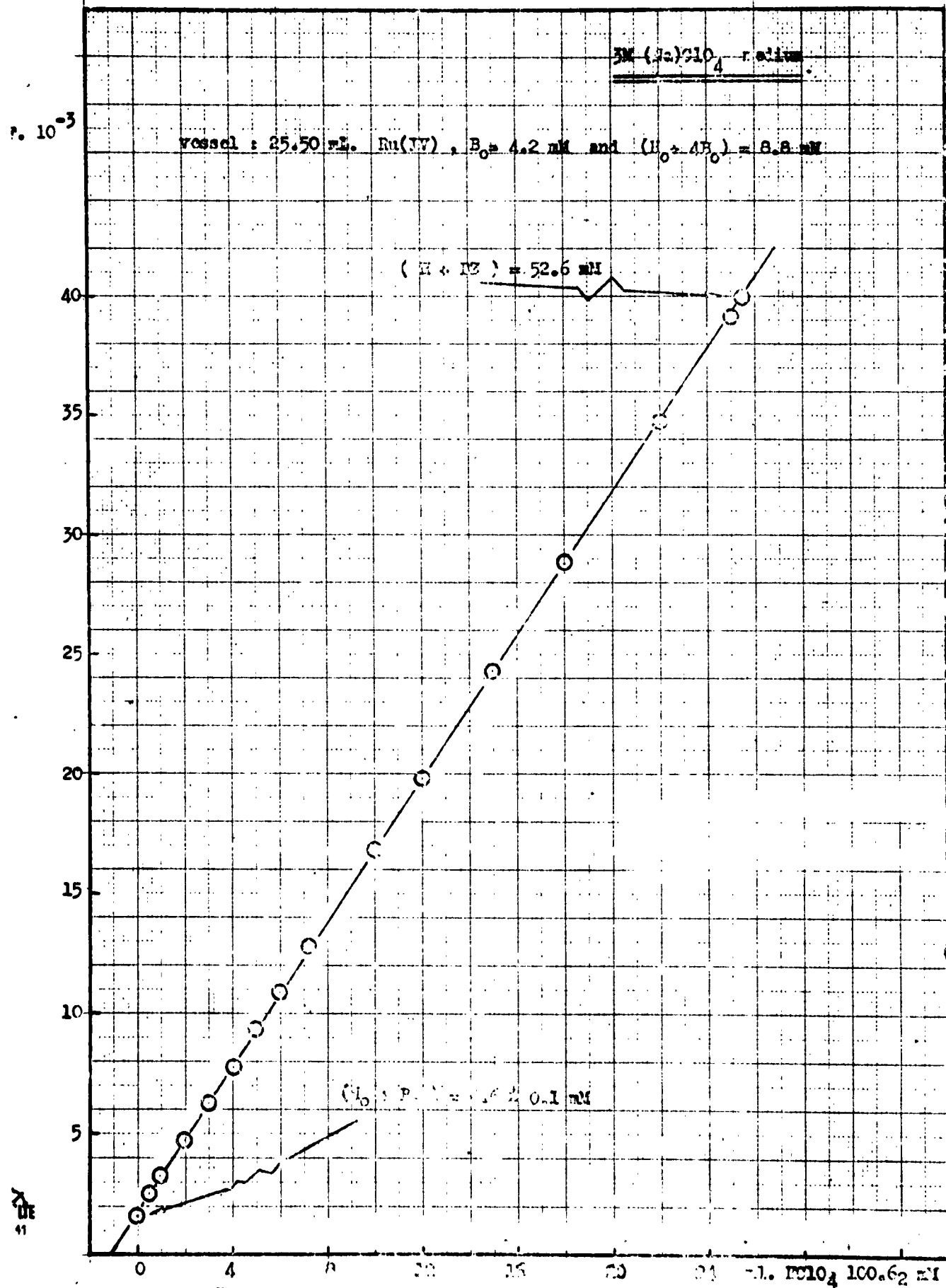


Fig. 7

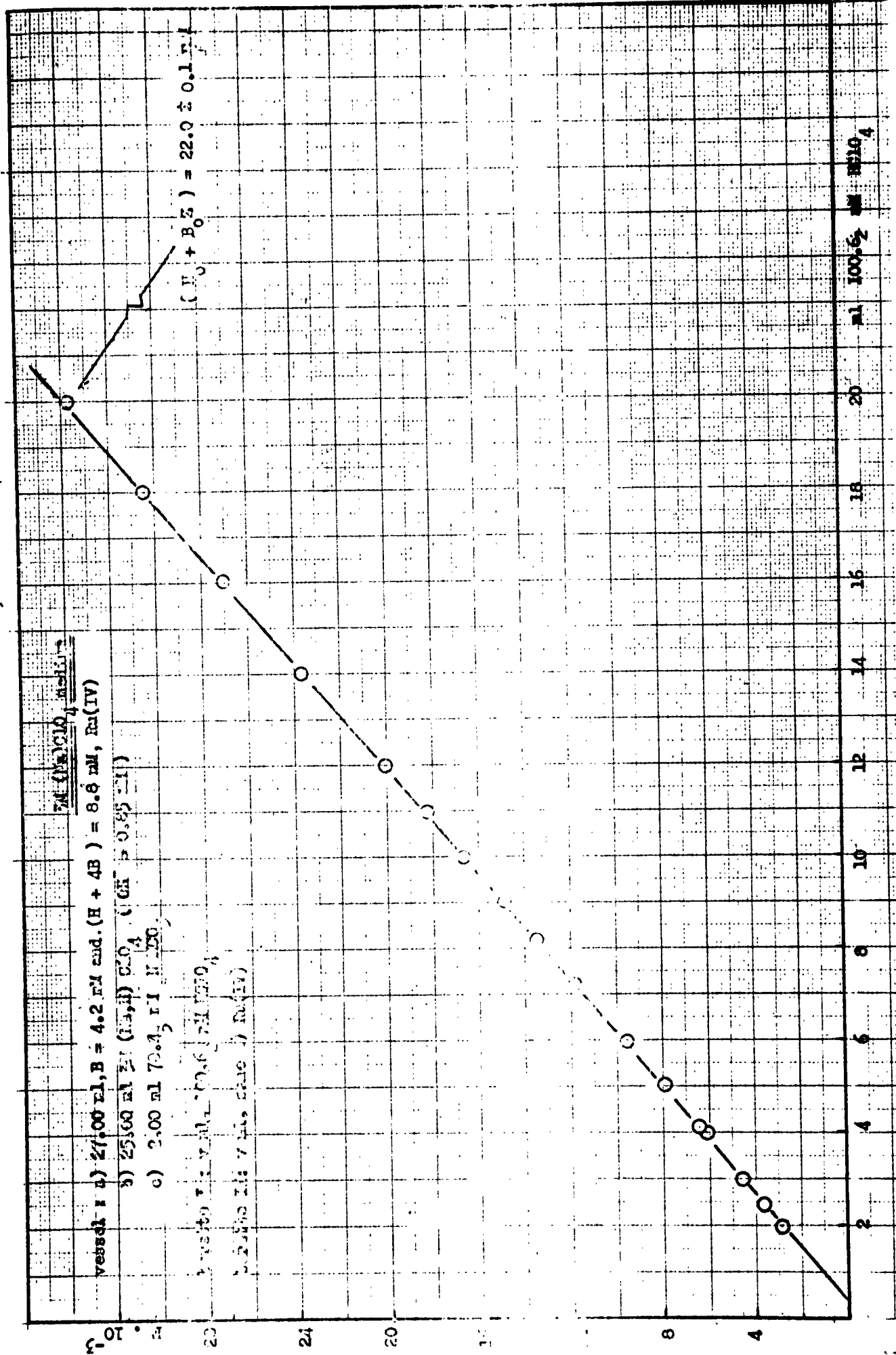


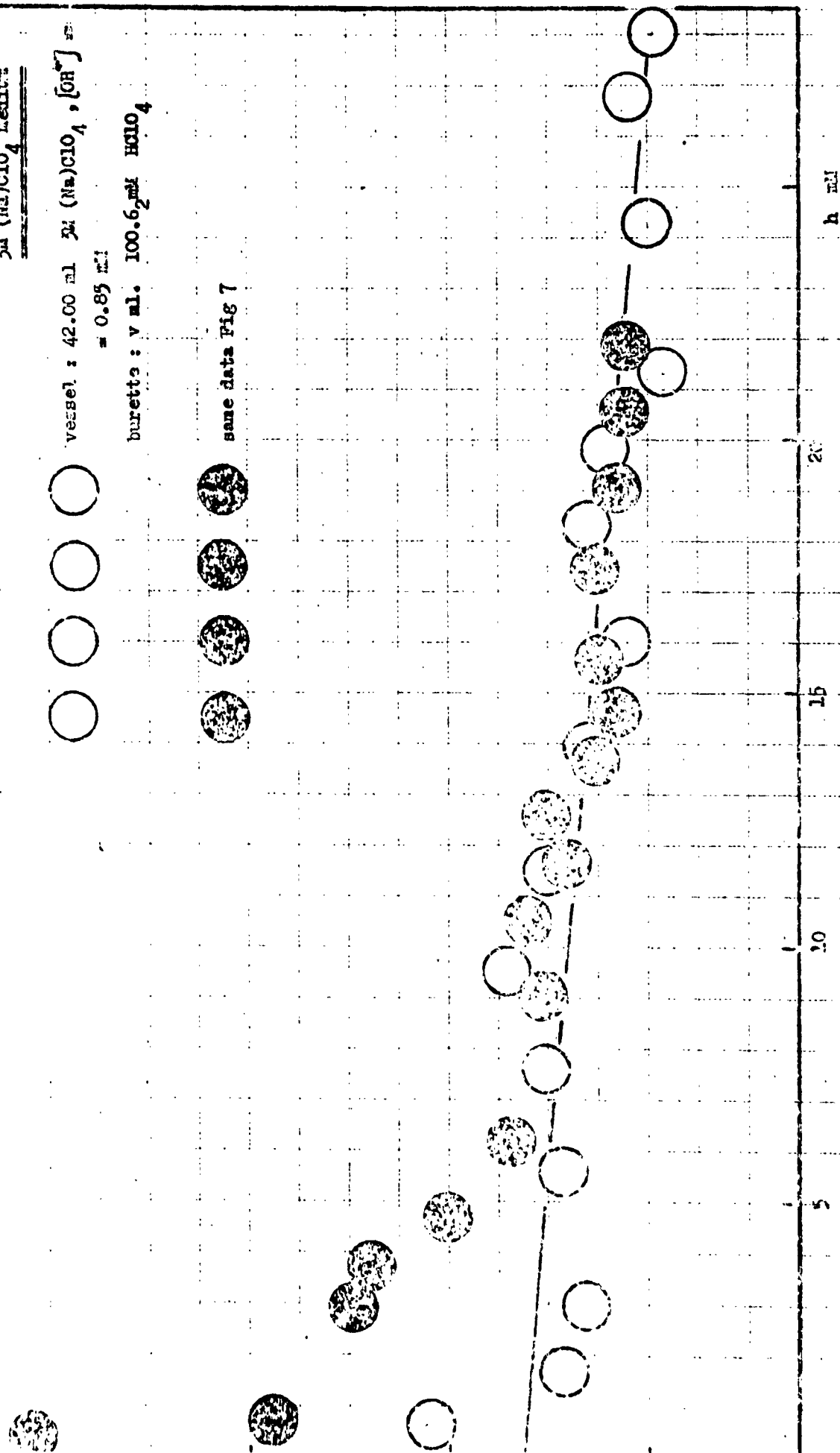
Fig. 8

3M (Na)ClO<sub>4</sub> medium

vessel : 42.00 ml 3M (Na)ClO<sub>4</sub>, [OH<sup>-</sup>] = 0.83 M

burette : v ml. 100.6<sub>2</sub>M HClO<sub>4</sub>

same data Fig 7





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ASTIA NO.

Contract No: AF 61 (052)-181

United States Air Force, Air Research and  
Development Command, European Office,  
Brussels, Belgium  
Technical Report

TITLE: RESEARCH ON CHARACTERISTICS OF TRANSITION  
ELEMENTS IN SOLUTION by Lars Gunnar Sillén

49 ( III+19+9+18 ) pages and 15 ( 7+8 ) Figures

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Royal Institute of Technology, Stockholm 70, Sweden  
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